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## GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

### VI. STRUCTURE-RETENTION INCREMENTS OF ALIPHATIC ESTERS

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#### SUMMARY

The influence of the polarity of the stationary phase on retention increments for the structural parameter of homologous series of aliphatic esters is detailed and the results are discussed in terms of the findings of earlier studies that have been reported where restricted ranges of solutes and solvents were considered.

#### INTRODUCTION

The gas chromatography of various aliphatic esters has been extensively studied and much retention data have been assembled in the ASTM<sup>1</sup> and other compilations<sup>2</sup> although the systematic study of retention and structure of homologous esters has not been exhaustively investigated.

Incremental increases of 100 index units per homolog containing five or more carbon atoms were reported for some ester series by Wehrli and Kováts<sup>3</sup>. Kováts<sup>4</sup> later stated that "in any homologous series the retention index of higher members increases by 100 index units per methylene group introduced". This implied quite erroneously that the slopes of the conventional data plots of all homologous series are the same although index contributions due to a methylene group of less than 90 index units had been reported earlier by Zulaica and Guiochon<sup>5</sup> for dibasic esters.

Retention indices of methyl esters of isomeric aliphatic monocarboxylic acids have been reported by Schomburg<sup>6</sup>. Relationships between retention, structure and boiling point of normal and branched-chain methyl esters were demonstrated. The equations of simple plots were determined and empirical relationships were reported that allowed calculation of either retention indices or boiling points of the esters using the particular experimental conditions. Subsequent work with methyl and ethyl esters of  $\alpha$ - and  $\beta$ -alkyl,  $\alpha, \beta, \gamma, \dots, \omega$ -methyl substituted carboxylic acid esters<sup>7</sup> allowed the formulation of rules for the elution sequence of different isomers by considering the retention behaviour on two standard non-polar phases.

A concept termed "homomorphy" which considered the retention difference of two substances differing by one or two structural elements was developed:

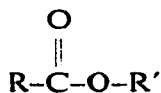
$$H^A = I_{(\text{substance})} - I_{(n\text{-paraffin})}$$

where  $H^A$  is the homomorphy factor. The value  $H^A$  with  $n$ -alkyl compounds is similar to the functional retention index (FRI) used earlier by Swoboda<sup>8</sup> in studies with esters:

$$\text{FRI} = H^A = I_{(\text{ester})} - I_{(\text{hydrocarbon skeleton})}$$

Values of  $H^A$  and retention index differences ( $\Delta I$ ) on polar and non-polar phases were shown for many ester structures and a consideration of  $H^A$  and  $\Delta I$  has subsequently been proposed for use in tentative identification<sup>9,10</sup>.

Earlier work from this laboratory has considered the retention behaviour of homologous esters, which were conveniently represented as



where the carbon numbers of the acid and alcohol chains are R and R', on SE-30<sup>11</sup> and with some other polysiloxane phases<sup>12,13</sup> where it was apparent that:

(1) The slopes of plots representing homologous esters with the same number of carbon atoms in the acid chain (R) decrease as the value of R is increased; similarly for the same number of carbon atoms in the alcohol chain (R') the slopes decreases as the value of R' increases with the phases considered.

(2) Retention of methyl esters follows boiling point.

(3) On stationary phases containing highly polarizable substituent groups it was evident that a loss of linearity occurs with alcohol ester plots.

(4) The effect of isomerization in the alcohol chain was most apparent with isopropyl esters and to lesser extents with isobutyl and isopentyl esters.

(5) It is apparent that the methylene group has a greater effect on retention when in the alcohol chain (R') than in the acid chain (R), this effect having also been observed with  $\alpha$ -alkyl acrylic esters<sup>14</sup>.

(6) Retention increments for the carboxyl group in  $n$ -alkyl esters indicated that the net retention of the group increased with increasing polar character of the phase.

The present study considers the simple structure-retention trends observed in our previous work in terms of statistically determined increments for the structural parameters present in the ester series, the range of compounds and stationary phases evaluated being greater than previously employed to provide carefully prepared data for further study of the substance polarity factors of Rohrschneider.

## EXPERIMENTAL

### *Gas chromatography*

The chromatography was carried out on a modified F&M 810/29 Research Chromatograph fitted with improved flow control and thermostatic column-oven controller. The oven temperature was independently monitored throughout the determinations with a calibrated thermocouple. The retention data were obtained isothermally at 150° using 12 ft.  $\times$  1/4 in. O.D. aluminium columns packed with 10% stationary phase on 62-72 mesh acid-washed and silanized Celatom. Flame ionization detection was used with the following conditions: injection temperature, 190°; detector temperature, 220°; carrier gas, helium; flow-rate, 30 ml/min with an inlet pressure of 45 p.s.i.

### *Stationary phases*

The stationary phases used were all polysiloxanes and could be separated into three basic classes depending on the type of substituent group. Class I consisted of non-polar phases, primarily containing alkyl groups, class II of the low- to medium-polarity donor phases, containing groups capable of exhibiting donor properties, and class III of the medium to polar acceptor phases, which contained substituents exhibiting acceptor properties.

The degree and type of substitution, as well as the classification of polarity in terms of Rohrschneider constants, for the polysiloxanes used are shown in Table I.

Low-molecular-weight polydiphenylsiloxane oligomers were prepared by conventional synthesis. Diphenyldichlorosilane containing less than 1% triphenylchlorosilane as chain terminator was hydrolysed by slowly dropping it into a 10% sodium carbonate solution. A reaction temperature of 25° was maintained to minimize any preliminary polymerization while the hydrogen chloride evolved was neutralized and the solid di- and triphenylsilanol formed were broken up.

The dry silanol mixtures were polymerized by heating a solution in toluene containing potassium hydroxide. The reaction was continued until water liberation ceased and further toluene was added to dissolve the low-molecular-weight products while the higher-molecular-weight species were essentially insoluble at room temperature. The soluble material was neutralized, freed of water and toluene and recovered as a white solid.

### *Preparation of esters*

The esters were largely of commercial quality and of substantial purity. Esters were prepared in the laboratory by conventional esterification or transesterification procedures using the macroreticular acidic ion exchanger Amberlyst 15.

## RESULTS AND DISCUSSION

The retention data of the esters examined are shown in Tables II and III as relative retention ( $V_R$ ) using *n*-nonane as standard and as retention indices ( $I_R$ ).

With SE-30, DC-230, DC-710 and diphenyl polysiloxane it is apparent that the retention behaviour of the esters on non-polar and donor phenyl phases is visually very similar, *i.e.* the separations (differences in intercepts) of the acid homologs are of similar magnitudes while the slopes of these homologs are similar, and decrease slightly as R increases; however, as expected, the retention values of the homologs increase with increasing polarity of the stationary phase.

With F-500, XE-60, XF-1150 and SILAR 5CP slight variations in retention behaviour occur as the stationary phase polarity is increased; the separation of the acid homologs is decreased, especially for the lower members of the series with the more polar stationary phases and similarly the slopes of the homologs tend to decrease with increased polarity as well as with increased R.

These effects are consistent with data for some of the esters on several non-polar or donor phases where the behaviour was stated to follow that of boiling point and on acceptor phases which have been described in terms of acceptor interaction<sup>13</sup>. The range of phases used previously was apparently not adequate to describe the phenomenon because low- to medium-polarity donor phenyl and medium-polarity acceptor

TABLE I  
COMPOSITION OF STATIONARY PHASES AND ROHRSCHEIDER CONSTANTS

Stationary phase	Supplier	Class	Methyl replacement	Rohrschneider constants				
				X	Y	Z	U	S
SE-30	General Electric (New York, N.Y., U.S.A.)	I	—	0.16	0.20	0.50	0.85	0.48
OV-7*	Ohio Valley Specialty Chemical Co. (Marietta, Ohio, U.S.A.)	II	20% phtenyl	0.42	0.81	0.85	1.52	0.89
DC-710*	Dow Corning (Midlands, Mich., U.S.A.)	II	50% phenyl	1.30	1.66	1.79	2.83	2.47
OV-25*	Ohio Valley Specialty Chemical Co.	II	75% phtenyl	1.76	2.00	2.15	3.34	2.81
100% Phenyl**	Laboratory prepared	II	100% phenyl	1.81	2.87	2.48	4.35	4.01
DC-230**	Dow Corning	I	stearyl	0.42	0.83	0.71	0.96	1.03
DC-530**	Dow Corning	II	6% aminoalkyl	0.63	2.69	1.29	2.04	1.16
XE-60*	General Electric	III	25% cyanoethyl	2.08	3.85	3.62	5.33	3.45
XF-1150**	General Electric	III	50% cyanoethyl	3.18	5.33	3.81	7.02	5.04
OV-225*	Ohio Valley Specialty Chemical Co.	III	25% phenyl 25% cyanoethyl	2.17	3.20	3.33	5.16	3.69
SILAR 5CP**	Applied Science Labs. (State College, Pa., U.S.A.)	III	50% phenyl 50% cyanoethyl	3.04	4.97	4.29	6.78	5.24
F-400**	Shin-Etsu (Tokyo, Japan)	III	<50% trifluoromethylbenzyl	0.63	1.30	1.69	2.09	1.73
F-500**	Shin-Etsu	III	50% trifluoromethylbenzyl	0.94	1.66	2.26	2.58	2.21
QF-1*	Dow Corning	III	50% trifluoropropyl	1.41	2.13	3.55	4.73	3.01

\* Determined by Supina and Rose<sup>14</sup>.

\*\* Determined in this laboratory.

TABLE II  
RETENTION DATA FOR NORMAL AND ISOMERIC SATURATED ESTERS AND STANDARD SUBSTANCES ON NON-POLAR AND DONOR PHASES

Compound	Stationary phase													
	SE-30		OV-7		DC-710		OV-25		100% Phenyl		DC-230		DC-530	
	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$
Benzene	0.296	674	0.360	719	0.471	767	0.675	830	0.800	860	0.309	688	0.423	733
Butanol	0.252	644	0.335	706	0.452	760	0.613	812	0.857	869	0.268	683	0.692	829
2-Pentanone	0.296	674	0.417	746	0.545	793	0.726	843	1.075	917	0.321	701	0.787	854
Nitropropane	0.378	718	0.671	832	0.946	892	1.373	961	1.825	1018	0.473	771	0.692	829
Pyridine	0.448	750	0.807	865	1.115	922	1.745	1005	2.857	1117	0.599	809	0.754	846
2-Methyl-2-pentanol	0.386	722	0.496	777	0.566	800	0.741	847	0.905	881	0.304	685	0.740	842
tert.-Butyl acetate	0.317	686	0.384	731	0.455	761	0.557	795	0.692	833	0.420	743	0.414	729
Methyl formate	0.062	386	0.082	453	0.104	496	0.166	571	0.225	618	0.070	419	0.120	488
Ethyl formate	0.112	495	0.142	552	0.172	586	0.262	655	0.373	715	0.123	521	0.199	587
Propyl formate	0.200	602	0.269	667	0.317	696	0.453	756	0.625	813	0.220	626	0.332	686
Butyl formate	0.356	707	0.486	774	0.579	804	0.761	852	1.021	907	0.400	734	0.571	792
Pentyl formate	0.621	810	0.873	879	1.054	912	1.312	952	1.650	998	0.697	835	0.921	885
Hexyl formate	1.059	907	1.492	976	1.832	1011	2.195	1047	2.699	1092	1.222	937	1.499	980
Isopropyl formate	0.153	552	0.190	604	0.226	635	0.310	686	0.458	754	0.147	553	0.239	622
Isobutyl formate	0.291	670	0.384	731	0.468	766	0.585	803	0.789	858	0.303	684	0.436	739
Isopentyl formate	0.521	777	0.704	840	0.845	872	1.073	915	1.350	958	0.560	795	0.766	849
Methyl acetate	0.121	509	0.148	559	0.195	609	0.322	693	0.409	732	0.122	519	0.182	569
Ethyl acetate	0.190	592	0.242	648	0.306	690	0.462	760	0.593	803	0.189	599	0.265	642
Propyl acetate	0.332	695	0.438	755	0.552	796	0.766	853	0.962	895	0.339	704	0.453	747
Butyl acetate	0.570	794	0.764	855	0.960	895	1.288	949	1.591	991	0.606	810	0.756	846
Pentyl acetate	0.969	891	1.357	958	1.690	996	2.161	1044	2.546	1081	1.077	914	1.235	942
Hexyl acetate	1.638	988	2.329	1056	2.879	1092	3.498	1133	4.136	1174	1.856	1012	2.041	1040
Isopropyl acetate	0.250	643	0.299	686	0.367	722	0.522	782	0.741	846	0.231	635	0.309	672
Isobutyl acetate	0.466	750	0.595	810	0.731	846	0.976	898	1.227	942	0.486	770	0.659	820
Isopentyl acetate	0.811	859	1.109	922	1.343	955	1.707	1001	2.068	1042	0.894	880	1.088	917

(Continued on p. 108)

TABLE II (continued)

Compound	Stationary phase													
	SE-30	OV-7	DC-710	OV-25	100% Phenyl	DC-230	DC-530							
	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$						
Methyl propionate	0.217	617	0.269	667	0.343	710	0.502	775	0.680	829	0.201	610	0.294	663
Ethyl propionate	0.328	692	0.411	743	0.515	783	0.732	845	0.909	885	0.316	692	0.437	740
Propyl propionate	0.556	789	0.746	851	0.906	884	1.220	934	1.477	977	0.556	792	0.712	835
Butyl propionate	0.942	886	1.290	949	1.579	984	2.029	1032	2.386	1069	0.976	896	1.188	934
Pentyl propionate	1.575	980	2.221	1047	2.731	1082	3.361	1125	3.977	1166	1.766	1003	1.947	1031
Hexyl propionate	2.628	1074	3.752	1142	4.609	1176	5.473	1215	6.318	1255	3.014	1100	5.182	1126
Isopropyl propionate	0.409	733	0.517	785	0.623	817	0.844	971	0.955	894	0.403	736	0.529	777
Isobutyl propionate	0.765	848	1.012	906	1.222	938	1.566	985	1.750	1010	0.785	857	0.971	895
Isopentyl propionate	1.319	948	1.852	1014	2.179	1042	2.717	1086	3.091	1118	1.416	963	1.692	1003
Methyl butyrate	0.345	702	0.468	767	0.576	803	0.829	868	1.023	907	0.368	719	0.477	757
Ethyl butyrate	0.522	778	0.704	840	0.865	876	1.171	931	1.409	968	0.557	794	0.688	828
Propyl butyrate	0.886	875	1.212	938	1.482	973	1.922	1022	2.227	1056	0.976	896	1.129	924
Butyl butyrate	1.481	969	2.085	1036	2.535	1069	3.161	1114	3.591	1147	1.679	994	1.853	1021
Pentyl butyrate	2.463	1062	3.538	1131	4.306	1164	5.156	1208	5.886	1241	2.857	1091	3.024	1116
Hexyl butyrate	4.095	1156	5.949	1225	7.256	1258	8.317	1292	9.432	1331	4.837	1186	4.877	1209
Isopropyl butyrate	0.658	820	0.867	878	1.014	905	1.332	955	1.523	983	0.696	835	0.829	864
Isobutyl butyrate	1.218	933	1.644	993	1.963	1023	2.424	1065	2.705	1093	1.354	955	1.506	981
Isopentyl butyrate	2.059	1029	2.870	1093	3.444	1124	4.112	1163	4.636	1196	2.356	1056	2.506	1080
Methyl pentanoate	0.611	807	0.837	871	1.027	907	1.373	961	1.675	1001	0.646	821	0.822	863
Ethyl pentanoate	0.894	876	1.230	941	1.498	975	1.941	1014	2.273	1060	0.976	896	1.163	930
Propyl pentanoate	1.499	971	2.082	1036	2.529	1069	3.162	1111	3.591	1147	1.675	994	1.872	1023
Butyl pentanoate	2.472	1063	3.508	1130	4.283	1163	5.167	1205	5.773	1237	2.840	1089	3.021	1116
Pentyl pentanoate	4.039	1155	5.807	1222	7.216	1257	8.392	1204	9.318	1329	4.801	1185	4.890	1210
Hexyl pentanoate	6.719	1247	9.900	1316	12.057	1349	13.520	1382	15.023	1420	8.057	1287	7.920	1304
Isopropyl pentanoate	1.106	915	1.453	971	1.724	1000	2.181	1046	2.523	1079	1.191	932	1.365	961
Isobutyl pentanoate	2.028	1027	2.776	1087	3.317	1117	3.961	1156	4.432	1187	2.297	1051	2.472	1077
Isopentyl pentanoate	3.600	1132	4.776	1185	5.774	1217	6.716	1253	7.455	1286	3.957	1150	4.056	1173
Methyl hexanoate	1.026	902	1.477	974	1.788	1006	2.308	1056	2.682	1091	1.148	925	1.353	960
Ethyl hexanoate	1.537	976	2.196	1045	2.596	1073	3.235	1118	3.614	1148	1.687	995	1.901	1026
Propyl hexanoate	2.491	1064	3.671	1138	4.306	1164	5.221	1207	5.818	1239	2.848	1090	3.060	1119

Butyl hexanoate	4.092	1156	6.160	1231	7.209	1256	8.431	1295	9.318	1329	4.783	1184	4.880	1209
Pentyl hexanoate	6.698	1246	10.360	1325	12.111	1349	13.652	1384	14.977	1419	8.022	1278	7.940	1304
Hexyl hexanoate	11.000	1337	17.314	1417	20.111	1440	21.814	1470	23.864	1508	13.435	1371	12.761	1397
Isopropyl hexanoate	1.833	1008	2.571	1074	2.953	1095	3.470	1131	4.091	1172	2.017	1028	2.210	1055
Isobutyl hexanoate	3.357	1119	4.885	1189	5.603	1211	6.466	1246	7.182	1279	3.514	1128	4.012	1171
Isopentyl hexanoate	5.567	1212	8.384	1287	9.636	1308	10.882	1342	11.955	1376	6.087	1228	6.533	1266
Methyl isobutyrate	0.283	665	0.363	823	0.462	764	0.614	812	0.750	848	0.292	677	0.372	708
Ethyl isobutyrate	0.406	732	0.541	893	0.671	831	0.865	875	1.015	906	0.452	757	0.535	779
Propyl isobutyrate	0.719	836	0.935	891	1.134	925	1.429	968	1.614	994	0.761	851	0.888	878
Butyl isobutyrate	1.202	931	1.592	987	1.921	1019	2.346	1059	2.682	1091	1.311	949	1.453	974
Pentyl isobutyrate	2.001	1024	2.692	1082	3.277	1115	3.937	1155	4.273	1180	2.227	1045	2.382	1070
Hexyl isobutyrate	3.321	1117	4.553	1177	5.497	1208	6.205	1238	6.932	1272	3.780	1141	3.888	1165
Isopropyl isobutyrate	0.529	780	0.661	829	0.744	849	0.931	889	1.136	927	0.531	786	0.641	814
Isobutyl isobutyrate	1.010	899	1.269	946	1.497	975	1.780	1008	2.046	1039	1.072	913	1.206	937
Isopentyl isobutyrate	1.699	994	2.190	1045	2.620	1075	3.069	1109	3.477	1141	1.833	1010	1.977	1034
Methyl isopentanoate	0.482	763	0.638	823	0.764	854	1.000	902	1.250	945	0.507	777	0.638	814
Ethyl isopentanoate	0.728	839	0.943	893	1.135	925	1.422	967	1.705	1005	0.768	853	0.904	881
Propyl isopentanoate	1.188	929	1.589	987	1.909	1018	2.338	1059	2.682	1091	1.297	948	1.473	976
Butyl isopentanoate	1.967	1021	2.674	1081	3.205	1111	3.814	1149	4.227	1178	2.206	1044	2.386	1070
Pentyl isopentanoate	3.236	1112	4.499	1174	5.381	1204	6.186	1238	6.932	1272	3.727	1139	3.868	1164
Hexyl isopentanoate	5.334	1204	7.523	1267	9.007	1296	9.985	1326	11.000	1361	6.287	1233	6.264	1258
Isopropyl isopentanoate	0.884	874	1.115	923	1.303	950	1.603	989	1.818	1017	0.940	889	1.075	915
Isobutyl isopentanoate	1.617	985	2.121	1039	2.488	1066	2.862	1096	3.205	1125	1.799	1007	1.949	1031
Isopentyl isopentanoate	2.728	1081	3.641	1136	4.310	1164	4.941	1196	5.409	1225	3.079	1104	3.210	1128
Methyl isohexanoate	0.887	875	1.199	936	1.461	970	1.882	1019	2.227	1056	0.957	892	1.144	927
Ethyl isohexanoate	1.287	943	1.749	1004	2.111	1036	2.602	1078	2.977	1111	1.409	963	1.593	992
Propyl isohexanoate	2.116	1035	2.928	1097	3.525	1128	4.156	1165	4.796	1202	2.363	1056	2.551	1083
Butyl isohexanoate	3.459	1125	4.879	1189	5.896	1220	6.668	1252	7.614	1290	3.967	1150	4.102	1176
Pentyl isohexanoate	5.660	1215	8.148	1281	9.869	1313	10.744	1340	12.273	1381	6.652	1244	6.599	1268
Hexyl isohexanoate	9.290	1306	13.601	1374	16.448	1404	17.237	1427	19.477	1470	11.139	1337	10.647	1361
Isopropyl isohexanoate	1.561	979	1.997	1028	2.397	1059	2.848	1095	3.364	1134	1.624	988	1.844	1020
Isobutyl isohexanoate	2.844	1089	3.870	1147	4.569	1175	5.104	1202	5.841	1240	3.187	1110	3.335	1135
Isopentyl isohexanoate	4.708	1181	6.613	1244	7.869	1272	8.588	1298	9.727	1337	5.502	1209	5.437	1231

(Continued on p. 110)

TABLE II (continued)

Compound	Stationary phase													
	SE-30		OV-7		DC-710		OV-25		100% Phenyl		DC-230		DC-530	
	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$
Methyl 2-methylpentanoate	0.787	853	1.028	908	1.267	945	1.606	989	2.158	1050	0.820	864	0.994	900
Ethyl 2-methylpentanoate	1.118	917	1.472	973	1.788	1006	2.269	1053	2.763	1097	1.180	930	1.371	962
Propyl 2-methylpentanoate	1.838	1009	2.435	1064	2.956	1097	3.550	1136	4.368	1184	2.000	1026	2.210	1055
Butyl 2-methylpentanoate	2.973	1097	4.093	1157	4.938	1189	5.669	1222	7.026	1275	3.330	1118	3.509	1145
Pentyl 2-methylpentanoate	4.854	1187	6.702	1246	8.154	1279	9.144	1310	11.053	1361	5.574	1212	5.635	1237
Hexyl 2-methylpentanoate	7.947	1277	11.106	1337	13.599	1370	14.763	1398	17.526	1449	9.317	1305	9.090	1331
Isopropyl 2-methylpentanoate	1.349	952	1.696	999	1.945	1021	2.356	1060	3.026	1114	1.391	960	1.593	992
Isobutyl 2-methylpentanoate	2.479	1064	3.248	1116	3.849	1144	4.500	1179	5.263	1220	2.707	1081	2.910	1109
Isopentyl 2-methylpentanoate	4.026	1153	5.416	1208	6.514	1238	7.256	1267	8.864	1319	4.539	1174	4.689	1202
Methyl 2-ethylbutyrate	0.753	845	0.975	899	1.192	934	1.519	979	2.079	1043	0.774	854	0.964	894
Ethyl 2-ethylbutyrate	1.098	914	1.435	969	1.730	1000	2.075	1037	2.692	1092	1.137	924	1.353	960
Propyl 2-ethylbutyrate	1.798	1005	2.688	1060	2.887	1092	3.438	1130	4.184	1176	1.935	1020	2.162	1051
Butyl 2-ethylbutyrate	2.910	1093	3.926	1150	4.764	1182	5.519	1217	6.684	1265	3.217	1112	3.431	1141
Pentyl 2-ethylbutyrate	4.747	1183	6.509	1241	7.928	1273	8.813	1303	10.579	1353	5.385	1205	5.497	1233
Hexyl 2-ethylbutyrate	7.769	1273	10.820	1332	13.170	1364	14.356	1393	16.790	1441	9.000	1298	8.869	1326
Isopropyl 2-ethylbutyrate	1.362	954	1.671	996	1.952	1022	2.331	1058	2.868	1104	1.322	951	1.602	993
Isobutyl 2-ethylbutyrate	2.428	1060	3.178	1112	3.754	1139	4.200	1167	5.158	1216	2.621	1075	2.880	1107
Isopentyl 2-ethylbutyrate	3.949	1149	5.258	1202	6.312	1232	7.094	1263	8.421	1310	4.401	1169	4.601	1198



TABLE III  
RETENTION DATA FOR SATURATED ESTERS AND STANDARD SUBSTANCES ON ACCEPTOR STATIONARY PHASES

Compound	Stationary phase													
	XE-60		XF-1150		OV-225		SILAR 5CP		F-400		F-500		QF-1	
	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$
Benzene	0.835	863	1.663	1014	0.966	898	1.630	998	0.384	720	0.491	761	0.642	802
Butanol	1.359	967	3.101	1146	1.424	977	2.531	1090	0.373	715	0.496	763	0.833	861
2-Pentanone	1.427	977	3.030	1139	1.483	986	2.519	1089	0.590	801	0.831	864	1.650	1017
Nitropropane	3.345	1159	8.350	1379	3.266	1150	6.630	1291	0.928	887	1.355	960	2.958	1151
Pyridine	2.699	1113	6.100	1289	3.178	1148	6.173	1275	0.893	880	1.244	943	2.175	1081
2-Methyl-2-pentanol	1.470	984	2.675	1115	1.424	978	2.333	1073	0.581	794	0.727	838	1.067	918
<i>tert.</i> -Butyl acetate	0.811	857	1.363	972	0.856	873	1.272	947	0.512	776	0.649	815	1.025	909
Methyl formate	0.294	641	0.656	817	0.339	682	0.525	762	0.136	509	0.179	563	0.392	689
Ethyl formate	0.501	754	1.000	907	0.483	755	0.841	860	0.221	604	0.291	658	0.583	780
Propyl formate	0.779	848	1.573	1003	0.814	862	1.325	955	0.369	705	0.486	751	0.918	883
Butyl formate	1.319	960	2.400	1092	1.356	967	2.175	1059	0.629	810	0.813	860	1.425	984
Pentyl formate	2.142	1064	3.756	1187	2.229	1070	3.475	1156	1.057	912	1.313	954	2.258	1089
Hexyl formate	3.461	1166	5.811	1279	3.585	1167	5.500	1252	1.764	1013	2.250	1059	3.500	1189
Isopropyl formate	0.515	760	1.087	924	0.525	772	0.875	869	0.278	649	0.383	712	0.733	832
Isobutyl formate	1.064	915	2.056	1059	1.068	918	1.763	1015	0.529	776	0.675	823	1.275	959
Isopentyl formate	1.799	1027	3.144	1149	1.839	1030	2.825	1113	0.893	879	1.150	928	1.992	1060
Methyl acetate	0.461	737	0.944	894	0.492	759	0.800	850	0.236	617	0.312	672	0.563	772
Ethyl acetate	0.667	815	1.213	927	0.712	835	1.136	923	0.336	687	0.446	742	0.812	855
Propyl acetate	1.088	920	1.878	1040	1.144	932	1.750	1013	0.586	796	0.754	845	1.283	960
Butyl acetate	1.760	1022	2.944	1135	1.839	1030	2.870	1116	0.989	899	1.258	945	2.025	1064
Pentyl acetate	2.814	1122	4.542	1227	3.025	1132	4.538	1212	1.643	999	2.086	1045	3.200	1169
Hexyl acetate	4.490	1221	6.833	1313	4.839	1229	7.025	1303	2.721	1098	3.450	1143	4.925	1267
Isopropyl acetate	0.755	842	1.222	949	0.729	840	1.088	914	0.429	735	0.533	777	0.983	899
Isobutyl acetate	1.417	976	2.322	1086	1.424	977	2.225	1063	0.804	859	1.013	903	1.742	1030
Isopentyl acetate	2.348	1086	3.744	1186	2.432	1087	3.675	1172	1.386	965	1.671	1001	2.733	1133

(Continued on p. 112)

TABLE III (continued)

Compound	Stationary phase													
	XE-60		XF-1150		OV-225		SILAR SCP		F-400		F-500		QF-1	
	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$
Methyl propionate	0.740	837	1.389	976	0.771	851	1.275	947	0.368	704	0.475	754	0.795	842
Ethyl propionate	0.980	897	1.734	1023	1.000	905	1.625	998	0.543	781	0.688	827	1.125	930
Propyl propionate	1.613	1003	2.678	1115	1.695	1013	2.625	1098	0.914	883	1.150	928	1.767	1033
Butyl propionate	2.588	1104	4.078	1204	2.754	1113	4.175	1195	1.524	984	1.917	1028	2.733	1133
Pentyl propionate	4.093	1202	6.189	1292	4.432	1211	6.550	1289	2.529	1083	3.167	1127	4.258	1234
Hexyl propionate	6.505	1300	9.333	1379	7.076	1307	10.063	1378	4.150	1181	5.158	1222	6.542	1332
Isopropyl propionate	1.093	920	1.733	1023	1.119	928	1.650	1001	0.654	818	0.833	864	1.350	972
Isobutyl propionate	2.074	1057	3.278	1158	2.153	1062	3.225	1141	1.243	944	1.583	990	2.442	1107
Isopentyl propionate	3.299	1156	5.111	1252	3.619	1169	5.275	1243	2.114	1048	2.667	1093	3.750	1205
Methyl butyrate	1.108	923	2.000	1053	1.177	938	1.913	1032	0.604	802	0.758	846	1.282	960
Ethyl butyrate	1.490	986	2.579	1107	1.580	999	2.475	1085	0.879	876	1.096	918	1.800	1037
Propyl butyrate	2.417	1089	3.856	1192	2.555	1098	3.875	1179	1.429	971	1.808	1017	2.773	1136
Butyl butyrate	3.814	1187	5.778	1278	4.059	1193	6.038	1272	2.364	1070	2.971	1114	4.255	1234
Pentyl butyrate	6.020	1284	8.700	1364	6.454	1288	9.313	1362	3.886	1168	4.867	1212	6.518	1331
Hexyl butyrate	9.476	1380	13.000	1449	10.261	1383	14.250	1451	6.343	1264	7.883	1306	9.900	1427
Isopropyl butyrate	1.667	1010	2.556	1105	1.740	1019	2.538	1091	1.046	910	1.338	957	2.127	1075
Isobutyl butyrate	3.103	1143	4.644	1232	3.235	1146	4.650	1217	1.939	1031	2.458	1077	3.755	1205
Isopentyl butyrate	4.966	1243	7.167	1323	5.286	1247	7.488	1316	3.264	1134	4.100	1177	5.709	1301
Methyl pentanoate	1.803	1027	3.089	1145	1.950	1042	3.075	1131	1.028	906	1.354	960	2.046	1067
Ethyl pentanoate	2.372	1085	3.822	1190	2.647	1105	3.888	1180	1.477	978	1.850	1021	2.836	1141
Propyl pentanoate	3.675	1179	5.767	1277	4.126	1196	6.025	1221	2.414	1074	3.004	1116	4.364	1240
Butyl pentanoate	5.892	1279	8.533	1360	6.496	1289	9.275	1361	3.944	1171	4.899	1212	6.582	1334
Pentyl pentanoate	9.241	1375	12.756	1445	10.185	1382	14.275	1451	6.435	1267	7.946	1307	10.009	1429
Hexyl pentanoate	14.414	1470	19.022	1530	16.143	1476	21.750	1539	10.449	1362	12.755	1400	15.118	1524
Isopropyl pentanoate	2.601	1105	3.811	1190	2.790	1116	3.900	1180	1.772	1014	2.211	1056	3.277	1174
Isobutyl pentanoate	4.793	1235	6.878	1315	5.118	1240	7.162	1307	3.242	1132	4.033	1174	5.714	1301
Isopentyl pentanoate	7.606	1333	10.489	1404	8.328	1340	11.450	1405	5.397	1233	6.704	1274	8.668	1397
Methyl hexanoate	2.926	1133	4.756	1237	3.135	1140	4.838	1225	1.681	1003	2.142	1050	3.110	1162
Ethyl hexanoate	3.980	1196	5.778	1278	4.269	1203	6.125	1275	2.421	1075	3.050	1119	4.208	1231
Propyl hexanoate	6.015	1283	8.611	1362	6.563	1295	9.363	1363	3.933	1173	4.908	1213	6.367	1326

Butyl hexanoate	9.340	1377	12.744	1445	10.244	1383	14.275	1451	6.372	1265	7.925	1307	9.527	1418
Pentyl hexanoate	14.507	1471	18.900	1529	16.059	1480	21.813	1539	10.375	1361	12.854	1402	14.500	1514
Hexyl hexanoate	22.552	1565	28.111	1613	25.101	1575	33.025	1626	16.783	1456	20.617	1494	21.624	1605
Isopropyl hexanoate	4.200	1207	5.800	1279	4.330	1206	6.150	1275	2.860	1108	3.592	1151	4.827	1263
Isobutyl hexanoate	7.557	1332	10.311	1400	8.050	1333	11.000	1397	5.204	1225	6.420	1265	8.350	1388
Isopentyl hexanoate	11.951	1430	15.644	1489	13.000	1432	17.525	1494	8.565	1323	10.792	1367	12.597	1482
Methyl isobutyrate	0.863	870	1.511	994	0.908	885	1.335	957	0.484	758	0.600	800	1.046	913
Ethyl isobutyrate	1.168	968	1.876	1039	1.160	935	1.775	1016	0.700	831	0.859	871	1.509	997
Propyl isobutyrate	1.875	1035	2.833	1127	1.924	1041	2.738	1107	1.161	930	1.425	970	2.227	1086
Butyl isobutyrate	2.927	1130	4.333	1217	3.076	1136	4.316	1201	1.902	1028	2.342	1067	3.436	1185
Pentyl isobutyrate	4.574	1225	6.467	1302	4.866	1230	6.721	1294	3.119	1125	3.813	1163	5.264	1283
Hexyl isobutyrate	7.231	1323	9.889	1392	7.656	1323	10.285	1383	5.098	1221	6.175	1258	7.982	1378
Isopropyl isobutyrate	1.275	953	1.878	1040	1.227	947	1.754	1014	0.832	865	1.000	900	1.655	1018
Isobutyl isobutyrate	2.490	1096	3.511	1172	2.420	1086	3.365	1149	1.586	992	1.950	1031	3.027	1156
Isopentyl isobutyrate	3.985	1196	5.333	1261	3.966	1188	5.421	1249	2.591	1088	3.154	1126	4.609	1252
Methyl isopentanoate	1.374	969	2.356	1088	1.454	982	2.225	1063	0.813	860	0.978	896	1.624	1014
Ethyl isopentanoate	1.852	1033	2.844	1128	1.950	1042	2.831	1114	1.133	926	1.460	975	2.226	1086
Propyl isopentanoate	2.916	1129	4.300	1215	3.092	1137	4.400	1206	1.951	1033	2.364	1069	3.385	1182
Butyl isopentanoate	4.542	1224	6.478	1302	4.899	1231	6.775	1296	3.168	1128	3.820	1163	5.155	1278
Pentyl isopentanoate	7.084	1318	9.644	1386	7.714	1325	10.463	1386	5.161	1224	6.211	1259	7.801	1372
Hexyl isopentanoate	11.108	1414	14.467	1472	12.101	1417	15.925	1474	8.354	1319	10.035	1353	11.801	1467
Isopropyl isopentanoate	2.000	1049	2.978	1138	2.168	1064	3.025	1127	1.421	970	1.729	1008	2.606	1122
Isobutyl isopentanoate	3.640	1177	5.267	1259	3.882	1184	5.338	1246	2.583	1088	3.171	1127	4.527	1248
Isopentyl isopentanoate	5.852	1278	7.978	1346	6.227	1281	8.488	1343	4.270	1187	5.225	1225	6.783	1341
Methyl isohexanoate	2.473	1094	4.044	1202	2.630	1104	3.845	1177	1.418	970	1.863	1022	2.678	1128
Ethyl isohexanoate	3.329	1158	4.767	1237	3.510	1163	4.702	1219	1.993	1037	2.625	1090	3.667	1200
Propyl isohexanoate	5.113	1249	7.256	1326	5.445	1253	7.357	1313	3.323	1137	4.233	1184	5.449	1290
Butyl isohexanoate	7.847	1340	10.778	1408	8.513	1345	11.262	1402	5.393	1232	6.813	1277	8.186	1383
Pentyl isohexanoate	12.118	1433	16.033	1498	13.360	1438	17.238	1490	8.797	1329	11.008	1371	12.370	1478
Hexyl isohexanoate	18.906	1527	23.889	1578	20.857	1529	26.191	1578	14.256	1424	17.667	1464	18.470	1569
Isopropyl isohexanoate	3.513	1169	4.889	1242	3.664	1172	4.929	1229	2.470	1079	3.113	1123	4.110	1226
Isobutyl isohexanoate	6.365	1296	8.689	1364	7.151	1309	8.738	1340	4.512	1197	5.638	1240	7.110	1351
Isopentyl isohexanoate	10.059	1393	13.178	1452	10.832	1394	13.691	1442	7.453	1296	9.300	1338	10.670	1444

(Continued on p. 114)

TABLE III (continued)

Compound	Stationary phase													
	XE-60		XF-1150		OV-225		SILAR 5CP		F-400		F-500		QF-1	
	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$	$V_R$	$I$
Methyl 2-methylpentanoate	2.044	1054	3.189	1152	2.193	1065	3.083	1131	1.262	947	1.546	986	2.203	1084
Ethyl 2-methylpentanoate	2.764	1118	3.811	1190	2.857	1121	3.762	1173	1.781	1015	2.169	1052	2.957	1151
Propyl 2-methylpentanoate	4.143	1204	5.778	1278	4.487	1213	5.869	1266	2.905	1111	3.500	1146	4.483	1246
Butyl 2-methylpentanoate	6.374	1296	8.465	1359	6.933	1303	8.893	1352	4.636	1203	5.599	1238	6.678	1337
Pentyl 2-methylpentanoate	9.852	1389	12.556	1442	10.815	1394	13.524	1440	7.498	1297	9.004	1332	10.042	1430
Hexyl 2-methylpentanoate	15.384	1483	18.689	1526	16.899	1486	20.500	1527	12.085	1391	14.417	1424	14.992	1522
Isopropyl 2-methylpentanoate	3.801	1121	3.833	1191	2.966	1128	3.821	1176	2.203	1056	2.521	1082	3.398	1183
Isobutyl 2-methylpentanoate	5.237	1254	6.944	1317	5.546	1257	6.976	1302	3.855	1166	4.682	1203	5.848	1307
Isopentyl 2-methylpentanoate	8.303	1352	10.356	1401	8.740	1350	10.881	1394	6.254	1262	7.583	1298	9.203	1410
Methyl 2-ethylbutyrate	2.000	1049	3.056	1143	2.059	1053	2.869	1116	1.157	930	1.459	974	2.042	1066
Ethyl 2-ethylbutyrate	2.813	1122	3.667	1182	2.748	1113	3.726	1171	1.683	1003	2.087	1045	2.822	1140
Propyl 2-ethylbutyrate	4.141	1204	5.678	1274	4.328	1206	5.726	1260	2.746	1100	3.384	1140	4.263	1234
Butyl 2-ethylbutyrate	6.338	1295	8.256	1353	6.706	1296	8.519	1343	4.418	1193	5.388	1231	6.381	1327
Pentyl 2-ethylbutyrate	9.899	1390	12.200	1436	10.445	1387	13.143	1434	7.122	1287	8.686	1325	9.542	1419
Hexyl 2-ethylbutyrate	15.303	1482	18.133	1520	16.303	1478	19.869	1520	11.505	1381	13.934	1417	14.254	1510
Isopropyl 2-ethylbutyrate	2.796	1120	3.867	1193	2.924	1125	3.786	1174	2.112	1040	2.496	1080	3.254	1173
Isobutyl 2-ethylbutyrate	5.220	1253	6.733	1310	5.336	1249	6.714	1294	3.693	1158	4.504	1196	5.678	1300
Isopentyl 2-ethylbutyrate	8.293	1352	9.978	1393	8.445	1343	10.524	1387	5.972	1253	7.265	1290	8.288	1386

cianoethyl- and trifluoropropyl-substituted phases were only considered. In this work a greater range of acceptor and low-polarity donor aminoalkyl phases was used. Previously, the only donor phases available were phenyl-substituted materials and consequently dramatic effects with polar solutes interacting with hydrocarbon groups would not be expected.

The effect of incremental changes in the alcohol chain  $R'$  for all stationary phases is shown in Table IV. It is apparent that the effect is maximized with the lower members and decreases as  $R$  increases, in agreement with an earlier report<sup>13</sup>.

TABLE IV  
EFFECT OF INCREMENTAL CHANGES IN THE ALCOHOL CHAIN FOR *n*-SATURATED ACID ESTERS

Stationary phase	Ester series					
	Formate	Acetate	Propionate	Butyrate	Pentanoate	Hexanoate
SE-30	105.0	99.6	96.1	94.6	92.3	90.2
OV-7	105.8	103.0	101.0	97.1	93.7	93.3
DC-710	108.6	101.7	99.7	96.0	94.0	92.0
OV-25	98.7	94.8	93.3	91.4	90.1	88.6
100% Phenyl	95.2	93.0	93.5	91.0	89.7	90.3
DC-230	104.5	105.1	103.7	98.9	96.2	94.3
DC-530	99.9	99.9	99.2	96.1	93.3	92.4
XE-60	105.2	102.3	101.6	99.2	97.0	91.9
XF-1150	92.5	93.5	89.6	85.7	84.8	83.5
OV-225	102.0	98.9	101.8	97.3	92.4	91.9
SILAR 5CP	98.7	97.3	97.0	92.4	91.2	88.0
F-400	101.2	103.9	100.7	97.5	96.4	95.0
F-500	98.4	100.9	100.0	97.9	95.4	94.3
QF-1	100.4	104.6	101.2	98.0	95.8	94.1

The methyl esters show a positive deviation, the only exception being methyl formate, which in many cases fits on a linear plot. This behaviour has been previously reported and, although the magnitude of this deviation was uncertain, on non-polar phases a relationship with boiling point was evident. The magnitude of the average methyl deviations increased considerably as the general polarity of the stationary phase was increased, *i.e.* SE-30 20.3, OV-7 22.4, DC-710 24.9, OV-25 27.2, 100% phenyl 34.0, DC-230 22.7, DC-530 25.9, XE-60 30.7, XF-1150 42.0, OV-225 34.1, SILAR 5CP 39.0, F-400 25.7, F-500 26.8, QF-1 20.6 index units. The trend is consistent with earlier reports<sup>13,15</sup> that suggested that the deviation of first members of homologous series, methyl and formate esters in this case, was due to the slightly polar terminal groups being adjacent to the polar carbonyl group, allowing the transmission of the effect of the dipole through a greater length in the molecule. This would increase the cohesive forces of these first-member molecules and raise their boiling points. Hence these methyl and formate esters should be more polarizable with polar phases, as well as there being less chance of steric hindrance.

When the number of carbon atoms in the acid chain ( $R$ ) was plotted against  $V_R$ , the results were as expected from the separations of the acid ester plots. These alcohol ester plots (methyl to hexyl esters) are shown in Figs. 1 and 2 on non-polar and

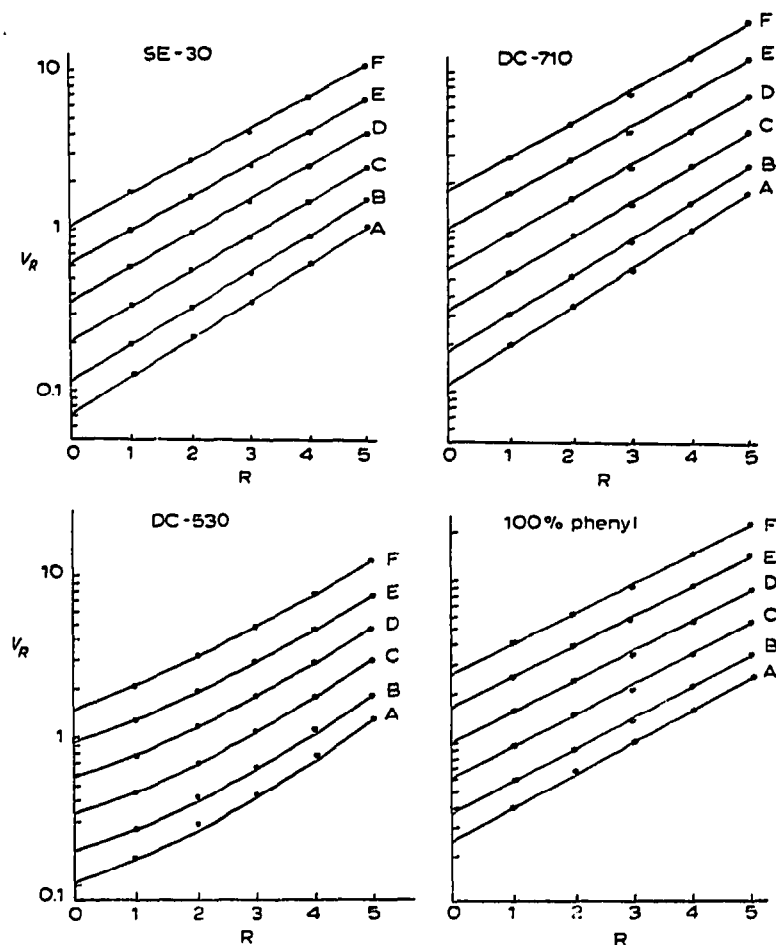


Fig. 1. Plots of logarithm of relative retention ( $V_R$ ) versus the number of carbon atoms ( $R$ ) in the acid chain of *n*-alkyl esters. A = Methyl; B = ethyl; C = propyl; D = butyl; E = pentyl; F = hexyl esters on non-polar and donor phases.

donor-substituted phases, *i.e.* SE-30, DC-710, 100% phenyl and DC-530, and on acceptor phases, *i.e.* F-400, F-500, XE-60 and SILAR 5CP. The most notable feature of these plots is that, if a sufficient concentration of highly polar groups, either acceptor or donor, is present in the stationary phase, then the plots tend to lose their linearity. However, those containing less polarizable groups, *i.e.* SE-30, DC-710 and 100% phenyl, but including some moderately polar phases, *i.e.* 100% phenyl, are linear together with F-400, which presumably contains insufficient highly polarizable acceptor groups to interact with the lower ester members. A further feature apparent from Figs. 1 and 2 is that the slopes of the ester series decrease when the polarity of the stationary phase increases, especially with phases containing highly polarizable groups, and when  $R'$  increases from methyl to hexyl. Both these effects are not as apparent as with the acid ester series plots owing to the loss of linearity.

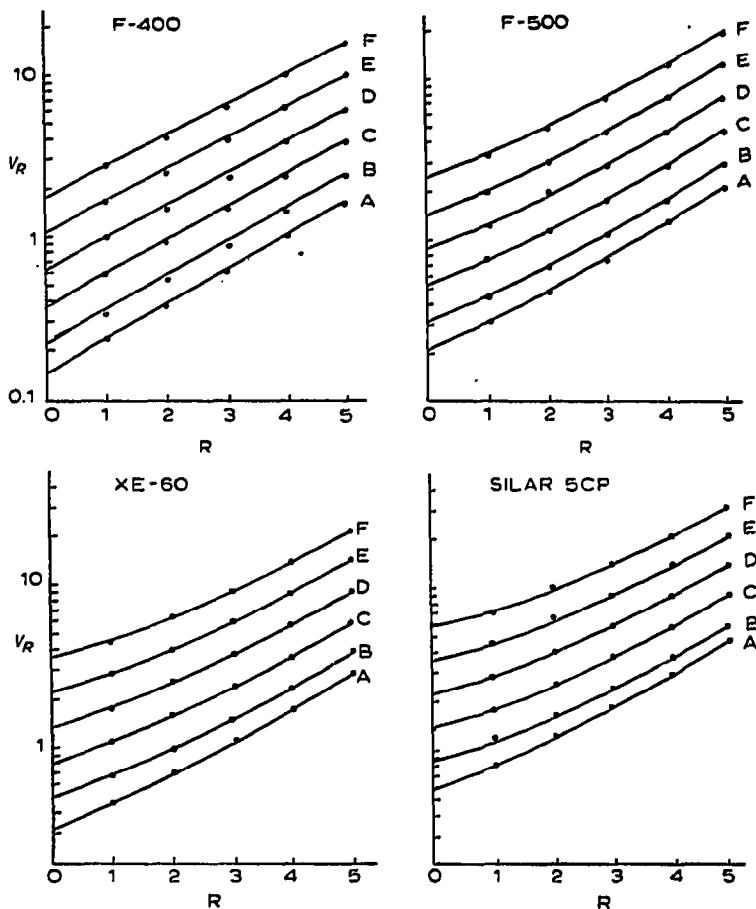


Fig. 2. Plots of logarithm of relative retention ( $V_R$ ) versus the number of carbon atoms ( $R$ ) in the acid chain of  $n$ -alkyl esters. A = Methyl; B = ethyl; C = propyl; D = butyl; E = pentyl; F = hexyl esters on acceptor phases.

The effect of the methylene increments in the acid chain of the alcohol ester series is shown in Table V, where the values are the slopes of the line of best fit for the homologs. They are not as meaningful as the values in Table IV for the acid ester series as in many instances the plots were non-linear, *i.e.* DC-530, XE-60, XF-1150, OV-225, SILAR 5CP, F-500 and QF-1. With these curvilinear plots, certain trends were still apparent. When  $R'$  increased the slopes or methylene increments decreased, as did the methylene increments with increased polarity of the stationary phase. The trend obtained here with polarity being more apparent than the trend obtained with polarity in Table IV indicates that the slopes of the  $V_R$  plots were less than those of the hydrocarbon plot for most stationary phases, although these values were not calculated owing to the loss of linearity and consequent lack of meaning. For donor and non-polar phases for which linear plots are obtained the values in Table IV are approximately 5 index units lower than the values in Table V for comparable esters. On stationary phases containing highly polarizable substituent groups the differences are

TABLE V

EFFECT OF INCREMENTAL CHANGES IN THE ACID CHAIN FOR *n*-SATURATED ALCOHOL ESTERS

Stationary phase	Ester series					
	Methyl	Ethyl	Propyl	Butyl	Pentyl	Hexyl
SE-30	103.5	93.8	91.4	89.0	86.8	85.9
OV-7	103.4	97.6	93.0	91.2	87.3	86.3
DC-710	101.6	94.8	90.8	88.9	86.5	85.3
OV-25	95.5	87.8	86.6	85.0	83.0	81.7
100% Phenyl	88.5	85.4	83.5	81.6	81.9	81.4
DC-230	100.4	99.3	97.4	93.5	90.1	91.1
DC-530	93.8	95.2	91.7	89.7	88.9	87.5
XE-60	95.8	89.9	86.3	85.4	84.1	82.7
XF-1150	81.5	81.3	78.8	74.9	72.6	75.5
OV-225	93.6	90.4	87.7	85.7	82.7	81.7
SILAR 5CP	92.0	85.8	85.5	81.2	79.0	78.1
F-400	97.9	97.3	92.5	90.2	88.9	87.5
F-500	96.8	92.8	90.2	88.7	87.1	85.5
QF-1	94.4	96.5	94.3	91.1	87.7	86.6

greater although it is evident with all phases that methylene groups have more effect in the alcohol chain,  $R'$ , than in the acid chain,  $R$ . A similar effect is observed when the boiling points of ester series are correlated with the carbon numbers ( $R$  and  $R'$ ).

From a study of molecular models, it is evident that the ether linkage hinders rotation of the alcohol chain. Hence incremental changes in this chain will have a slightly greater effect on molecular shape, maximizing the possible surface area owing to lack of rotation and thus increasing the cohesive forces of the molecule<sup>16</sup>. This may further explain the non-linearity of the alcohol ester plots, as incremental changes in the acid chain will have a greater effect on steric hindrance, as the lower members will be less likely to hinder the carboxyl group to the extent of the higher members in this chain and are more likely to exhibit an increased retention, especially with highly polarizable stationary phases. On the other hand, incremental changes in the alcohol chain, which have less chance of steric hindrance, will behave normally. Similarly, it has been reported<sup>13</sup> that ether linkages may allow a better transmission of the induced dipole between the methyl group and the polar carbonyl group and this increased polarization may exhibit an increase in retention for alcohol ester series. This differential incremental behaviour is most probably a compromise between electronic interactions and steric hindrance, both in the alcohol chain.

The effect of isomerism in the acid and alcohol chains has been previously reported for simple esters and, while the magnitude of the effects is less clear, values for the deviation in the acid chain of fatty acids have been extensively studied by Ackman<sup>17</sup>. The effect of isomerism in the alcohol chain is shown in Fig. 3 for isopropyl, isobutyl and isopentyl esters in relation to the saturated esters on SE-30, OV-25, OV-225 and XF-1150 where essentially the same behaviour is apparent for all phases and ester series with regard to isomeric deviations. The average magnitudes of the deviations are shown in Table VI for each stationary phase. It is apparent that the isopropyl esters have the largest deviation followed by the isobutyl and isopentyl esters. This is



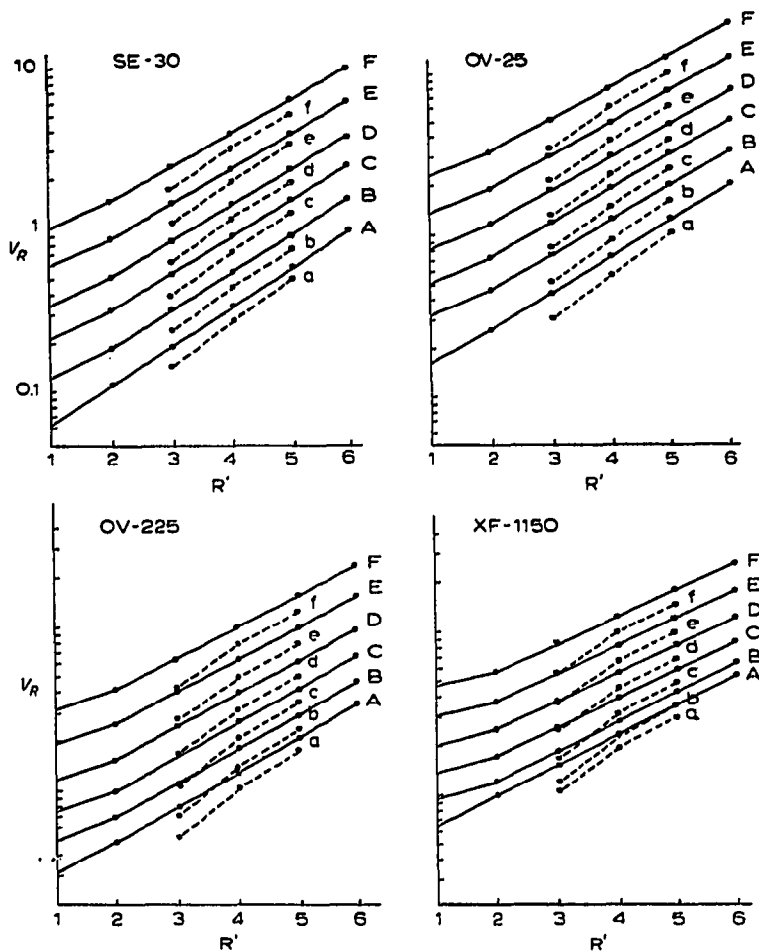


Fig. 3. Retention behaviour of isomeric alcohol esters. A to F are as in Fig. 1 and a to f are isoalkyl formates, acetates, propionates, butyrates, pentanoates and hexanoates, respectively.

expected, as when branching occurs the shape of the molecule approaches a sphere and the surface area is reduced to a minimum, the intermolecular forces thus being overcome at a lower temperature, with a lowering of the boiling point<sup>16</sup>. With isopropyl esters this effect will be maximized, decreasing with isobutyl and further with isopentyl esters. The effect of polarity on isomeric deviation is to increase these deviations, *i.e.* the retention of these iso esters is retarded, in relation to the saturated esters. This retardation is apparently due to the steric hindrance of the carboxyl group, demonstrated by the fact that the negative deviation with the most polar phase, XF-1150, for isopropyl esters is 54.9% higher than its deviation on SE-30 while isobutyl and an isopentyl ester are only 28.1% and 28.6% higher than those on SE-30, respectively, indicating that the carboxyl group is shielded to the greatest extent with the former structure.

The effect of isomerism in the acid chain may be observed in Fig. 4 on SE-30,

TABLE VI  
ISOMERIC DEVIATIONS FOR ALCOHOL ESTER SERIES

Stationary phase	Ester series		
	Isopropyl	Isobutyl	Isopentyl
SE-30	-55.6	-36.2	-31.8
OV-7	-65.4	-43.4	-36.6
DC-710	-69.1	-46.4	-40.2
OV-25	-74.4	-46.1	-40.2
100% Phenyl	-66.6	-52.0	-42.9
DC-230	-63.6	-40.9	-37.7
DC-530	-62.4	-38.7	-31.5
XE-60	-80.4	-45.6	-40.0
XF-1150	-86.1	-46.4	-40.9
OV-225	-85.4	-48.9	-43.3
SILAR 5CP	-88.4	-53.5	-44.9
F-400	-62.4	-38.1	-34.6
F-500	-61.2	-38.1	-33.5
QF-1	-62.8	-31.1	-30.2

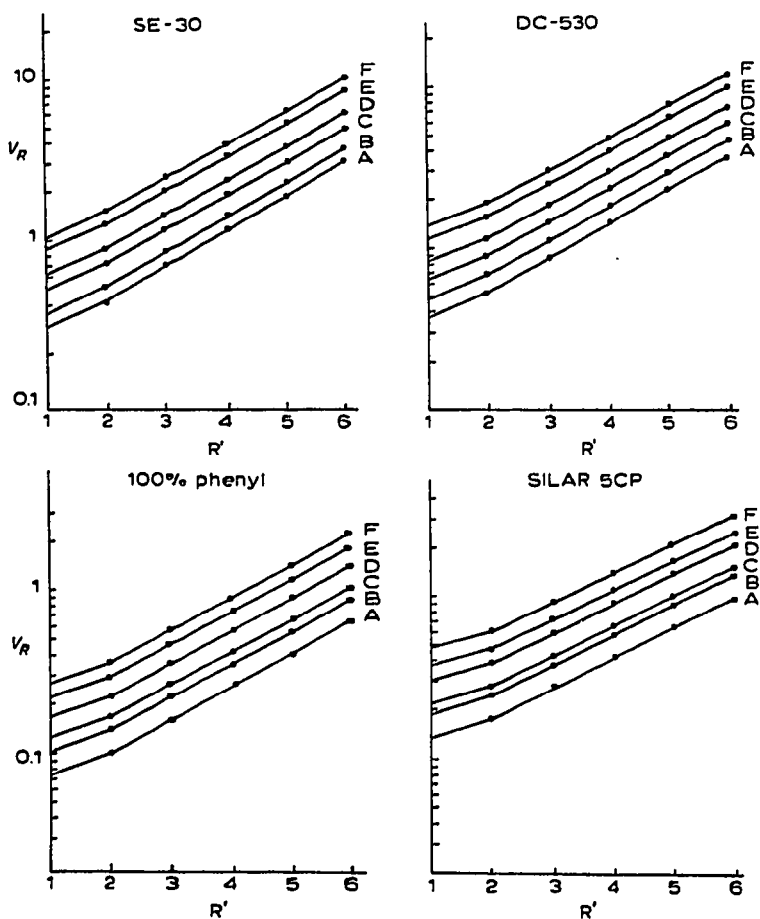


Fig. 4. Retention behaviour of isomeric acid esters. A = Isobutyrate; B = butyrate; C = isopentanoate; D = pentanoate; E = hexanoate; F = isohexanoate esters.

TABLE VII  
ISOMERIC DEVIATIONS FOR ACID ESTER SERIES

Stationary phase	Acid ester series				
	Isobutyrate	Isopentanoate	Isohexanoate	2-Methyl-pentanoate	2-Ethyl-butyrates
SE-30	-39.0	-41.1	-30.8	-58.2	-61.8
OV-7	-48.4	-48.5	-42.5	-75.8	-81.1
DC-710	-48.7	-52.0	-36.1	-68.2	-74.3
OV-25	-52.9	-55.9	-42.9	-72.2	-79.3
100% Phenyl	-59.8	-57.2	-38.0	-55.5	-62.8
DC-230	-44.6	-45.4	-33.8	-65.5	-71.9
DC-530	-46.6	-46.5	-34.9	-65.2	-69.0
XE-60	-56.6	-54.5	-36.9	-80.7	-80.2
XF-1150	-62.9	-59.6	-36.3	-86.1	-91.9
OV-225	-56.5	-57.4	-40.6	-83.0	-90.1
SILAR 5CP	-69.8	-66.3	-49.9	-98.9	-105.4
F-400	-42.5	-43.5	-33.7	-62.6	-73.0
F-500	-48.6	-47.9	-30.1	-68.8	-74.4
QF-1	-47.9	-56.7	-35.2	-81.9	-92.8

DC-530, 100% phenyl and SILAR 5CP stationary phases for isobutyrate, isopentanoate and isohexanoate ester series. The effect may be found in Table VII for these ester series plus 2-methylpentanoate and 2-ethylbutyrate ester series for all stationary phases. The behaviour exhibited here is not identical to the pattern found for isomerism in the alcohol chain. Predictably, the 2-ethylbutyrate esters show the greatest deviation followed by the 2-methylpentanoates, which, owing to the presence of the adjacent ethyl and methyl groups, are capable of shielding the carboxyl group quite severely<sup>9</sup>. However, the deviations of the isobutyrate and isopentanoate esters were of a similar magnitude, and in many cases the isopentanoates exhibited a greater deviation, while the isohexanoates exhibited least deviation. This anomaly is to be expected from boiling-point differences, as ethyl isobutyrate differs by 9° from ethyl butyrate, while ethyl isopentanoate and ethyl isohexanoate differ by 11° and 5° from their respective normal ethyl esters. The reason for this behaviour concerns the shape and steric hindrance of the molecules. Both the isobutyrate and isopentanoate molecules are compact molecules of approximately similar shapes and hence exhibit a similar ratio of surface areas. The isopentanoate molecule is capable of shielding the carbonyl group of the ester to a similar or even greater extent than the isobutyrate molecules. Thus it is probable that the cohesive forces per carbon atom of these two isomeric series will be similar and lower than their normal equivalents. The isohexanoate molecule, on the other hand, is not as compact a molecule, or capable of comparable shielding of the carboxyl group, hence its behaviour is similar to isopentyl ester structure exhibited in the alcohol chain.

When the polarity of the phases was increased, in general, the negative deviation due to isomerism in the acid chain increased, especially for the molecules that were capable of sterically hindering the polar carboxyl group. The greatest deviations were found for the 2-ethylbutyrates, which on polar XF-1150 exhibited 105.4 units deviation, *i.e.* they behaved similarly to *n*-pentanoates. Two other isomeric series,

isobutyrate and isopentanoate as well as the 2-ethylbutyrate and 2-methylpentanoate, exhibited between 45–50% greater negative deviation on the most polar phases (XF-1150 and SILAR 5CP) than on SE-30, the least polar phase. The remaining series, the isohexanoate, exhibited about 20% greater deviation on polar phases, indicating that it was a less sterically hindered molecule than the other branched-chain acid series considered here.

The retention increment due to the carboxyl group of the *n*-alkyl esters on various stationary phases was found as the intercept of the linear relationship, *i.e.*  $R = R' = 0$ , calculated from the line of best fit determined by regression analysis of an ester plot where  $R = R'$ .

The results obtained are shown in Table VIII together with values previously reported<sup>11,13</sup>, which were obtained from graphical extrapolations and which have been re-calculated by regression analysis.

TABLE VIII  
THE RETENTION INCREMENT OF THE CARBOXYL GROUP OF *n*-ALKYL ESTERS

Stationary phase	Previously reported <sup>11,13</sup>		Experimentally determined
	Graphical method	Regression method	
SE-30	304	307	324
Gensil S2116	275	265	—
OV-7	—	—	363
F-61	353	374	—
OV-17	410	421	—
DC-710	—	—	417
OV-25	550	501	507
85% Phenyl	495	517	—
100% Phenyl	—	—	548
DC-230	—	—	320
DC-530	—	—	377
XE-60	520	535	539
XF-1150	641	670	718
OV-225	—	—	558
SILAR 5CP	—	—	663
F-400	—	—	417
F-500	—	—	473
QF-1	541	575	571

The values determined are in reasonable agreement with values calculated in the same manner from an earlier report<sup>13</sup>. The value for SE-30 as expected is somewhat greater than the value of 290 units reported by Zulaica and Guiochon<sup>5</sup> for dibasic esters using SE-30 at 220°.

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## REFERENCES

- 1 O. E. Schupp and J. S. Lewis (Editors), *Gas Chromatographic Data Compilation*, Special Technical Publication DS25A, American Society for Testing Materials, Philadelphia, Pa., 2nd ed., 1967.
- 2 W. O. McReynolds, *Gas Chromatographic Retention Data*, Preston Technical Abstracts Co., Evanston, Ill., 1966, pp. 144, 145.
- 3 A. Wehrli and E. Kováts, *Helv. Chim. Acta*, 42 (1959) 2709.
- 4 E. Kováts, *Advan. Chromatogr.*, 1 (1965) 229.
- 5 F. T. Zulaica and G. Guiochon, *Bull. Soc. Chim. Fr.*, 1 (1963) 1242.
- 6 G. Schomburg, *J. Chromatogr.*, 14 (1964) 157.
- 7 G. Schomburg, *Separ. Sci.*, 1 (1966) 339.
- 8 P. A. T. Swoboda, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworth, London, 1962, p. 273.
- 9 G. Schomburg, *Advan. Chromatogr.*, 6 (1968) 211.
- 10 G. Schomburg and G. Dielmann, *J. Chromatogr. Sci.*, 11 (1973) 151.
- 11 R. W. Germaine and J. K. Haken, *J. Chromatogr.*, 43 (1969) 33.
- 12 I. D. Allen and J. K. Haken, *J. Chromatogr.*, 49 (1970) 409.
- 13 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 60 (1971) 33.
- 14 J. K. Haken, T. R. McKay and P. Souter, *J. Gas Chromatogr.*, 3 (1965) 61.
- 15 W. I. Waters, *Physical Aspects of Organic Chemistry*, Routledge and Kegan Paul Ltd., London, 5th ed., 1953, pp. 265-289.
- 16 R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Allyn and Bacon, Boston, Mass., 2nd ed., 1966.
- 17 R. G. Ackman, *J. Chromatogr. Sci.*, 10 (1972) 243; and references therein.
- 18 W. R. Supina and L. P. Rose, *J. Chromatogr. Sci.*, 8 (1970) 214.