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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

PART III. INFLUENCE OF STATIONARY PHASE POLARITY ON
RETENTION OF ALIPHATIC ESTERS

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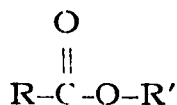
SUMMARY

The retention behaviour of a number of series of saturated homologous esters on polysiloxane stationary phases of increasing polar character is reported.

INTRODUCTION

The retention behaviour of homologous saturated esters on the essentially non-polar Methyl Polysiloxane SE-30 stationary phase has been reported¹. With little hydrogen bonding occurring, retention was primarily related to the boiling point of the esters. The familiar deviation of the retention of the methyl esters from a linear relationship with carbon number was observed while a similar effect was apparent with isopropyl esters. These variations were largely attributed to the generally higher and lower boiling points, respectively, of the methyl and isopropyl esters with respect to the other members of the homologous series rather than to any column effect.

The esters were conveniently represented as



where the carbon numbers of the acid and alcohol chains are R and R', respectively.

The data of homologous esters on an SE-30 stationary phase when considered with regard to boiling point showed the following features common to retention behaviour:

(1) The slopes of plots representing esters with the same number of carbon atoms in the acid chain (R) decreases as the value of R increases.

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(2) The methyl esters have slightly higher boiling points than expected from the slopes of the corresponding ester plots, while that of methyl formate shows a linear relationship with the alkyl formates.

(3) The isobutyl and isopentyl esters have boiling points relatively constantly lower than the corresponding *n*-alkyl esters, while the slopes of the boiling point plots of these series are parallel to those of the *n*-alkyl esters.

(4) The isopropyl esters have boiling points lower than expected from the slopes of the plots of the higher isoesters.

(5) The boiling points of esters where either R or R' or both of them have branched chains similarly tend to follow the retention behaviour.

In this work the retention behaviour of aliphatic esters with R and R' varying between 0 and 6 and between 1 and 8, respectively, on silicone stationary phases of increasing polar character is reported and the results are compared with the earlier observations¹.

The gas chromatography of aliphatic esters has been extensively documented² and systematic studies relevant to this work have been previously reviewed¹.

EXPERIMENTAL

Preparation of esters

The esters where available were of commercial quality and of substantial purity. The remainder of the esters were prepared in the laboratory using conventional esterification or transesterification procedures and were purified before use.

Stationary phases

The stationary phases were all polysiloxanes. The Methyl Silicone Polymer SE-30 without effective polar groups on the polymer chain can be considered as essentially non-polar.

TABLE I

ROHRSCHEIDER CONSTANTS OF STATIONARY PHASES

<i>Phase</i>	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>U</i>	<i>S</i>
SE-30	0.16	0.20	0.50	0.85	0.48
OV-17	1.30	1.66	1.79	2.83	2.47
OV-25	1.76	2.00	2.15	3.34	2.81
XE-60	2.08	3.85	3.62	5.33	3.45

Replacement of methyl groups by polar or polarisable substituents allows an increase in the polarity factor of the stationary phase. The polysiloxanes OV-17 and OV-25 containing 50 and 75% phenyl groups based on substitution of methyl groups in a dimethyl-polysiloxane polymer have been used together with XE-60 with a 50% replacement of methyl groups by cyanoethyl groups.

Classification of stationary phase characteristics in terms of Rohrschneider constants for the polysiloxanes used³ is shown in Table I.

Gas chromatography

The retention data were obtained on a modified F & M 810/29 Research Chromatograph with simultaneous flame ionisation and thermal conductivity detection and fitted with an improved flow control system. Two 12 ft. \times $\frac{1}{4}$ in. O.D. aluminium columns were packed with 10% of the stationary phase on 60–80 mesh acid-washed and silanised Celite 560 and operated isothermally at 150°.

With thermal conductivity detection the following conditions were used: injection temperature, 190°; detector temperature, 220°; bridge current, 150 mA; carrier gas, helium; flow rate, 65 ml/min with an inlet pressure of 40 p.s.i.

The retention data of the esters examined are shown in Table II as net retention (V_R), relative retention (V_R) using nonane as standard, and as retention indices (I_R).

DISCUSSION AND RESULTS

Plots of the logarithm of the relative retention volume against the number of carbon atoms in the alcohol chain (R') for the normal and isoesters produced a series of linear relationships for each of the stationary phases. Plots of the esters examined on OV-25 are shown in Fig. 1.

Positive and negative deviations from linearity existed with the methyl and isopropyl esters on all four stationary phases. With SE-30 and OV-17 the slopes of the plots decreased as the number of carbon atoms in the acid chain increased, *i.e.* R equals 0 to 3, after which the plots are parallel. With OV-25 the greatest slope was observed with the acetate esters while the formate and propionate esters produced

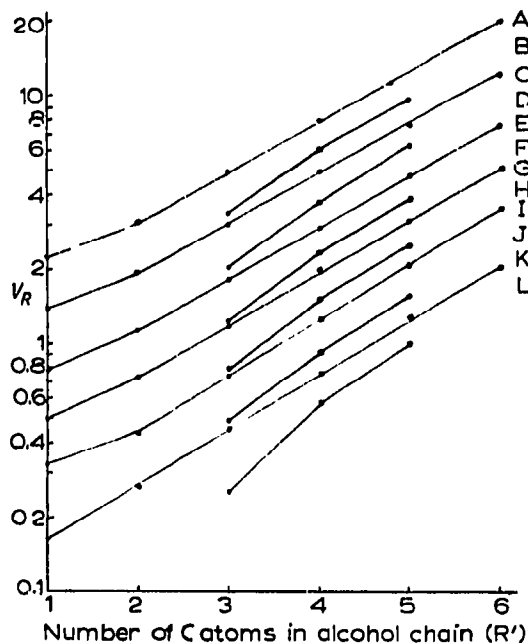


Fig. 1. Plots of the logarithm of the relative retention volume *versus* the number of carbon atoms in the alcohol chain of saturated esters on OV-25 stationary phase with varying alcohol chain (R') length with R' forming both normal and isoesters while the acid chain (R) is linear.

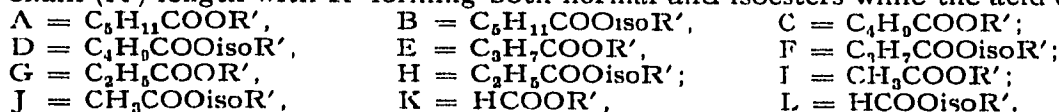


TABLE II
RETENTION DATA FOR ALIPHATIC ESTERS
(a) corrected for dead volume, (b) relative to nonane.

Ester	Stationary phase											
	SE-30		OV-17		OV-25		XE-60					
	$V_g(a)$	$V_R(b)$	I_R	$V_g(a)$	$V_R(b)$	I_R	$V_g(a)$	$V_R(b)$	I_R			
Methyl formate	0.050	0.075	380	0.037	0.123	493	0.036	0.170	542	0.057	0.350	653
Ethyl formate	0.085	0.129	487	0.066	0.220	650	0.055	0.260	631	0.090	0.560	766
Propyl formate	0.145	0.216	592	0.150	0.380	711	0.090	0.450	740	0.130	0.810	851
Isopropyl formate	0.105	0.162	528	0.375	0.125	494	0.054	0.250	624	0.090	0.560	766
Butyl formate	0.250	0.375	703	0.250	0.630	811	0.160	0.774	840	0.210	1.310	966
2-Methylpropyl formate	0.200	0.301	660	0.110	0.370	705	0.120	0.566	788	0.168	1.040	912
Pentyl formate	0.425	0.645	812	0.410	1.03	905	0.275	1.28	949	0.330	2.060	1070
3-Methylbutyl formate	0.350	0.512	774	0.195	0.650	816	0.215	1.00	894	0.265	1.660	1026
Hexyl formate				0.710	1.79	1013	0.450	2.04	1042	0.490	3.060	1164
Octyl formate				1.480	4.93	1216	1.210	5.50	1244	1.17	7.310	1365
Methyl acetate	0.093	0.140	506	0.080	0.260	632	0.071	0.330	678	0.080	0.500	741
Ethyl acetate	0.130	0.200	571	0.100	0.360	697	0.090	0.440	731	0.110	0.69	816
Propyl acetate	0.225	0.338	683	0.180	0.580	795	0.160	0.780	849	0.170	1.07	918
Isopropyl acetate	0.170	0.259	625	0.115	0.390	716	0.105	0.490	745	0.125	0.78	844
Butyl acetate	0.375	0.585	787	0.300	0.970	895	0.260	1.21	938	0.260	1.63	1024
2-Methylpropyl acetate	0.310	0.468	750	0.240	0.800	857	0.105	0.490	745	0.213	1.32	966
Pentyl acetate	0.645	0.980	898	0.480	1.60	993	0.435	2.00	1040	0.400	2.50	1118
3-Methylbutyl acetate	0.525	0.798	854	0.390	1.30	952	0.335	1.56	990	0.335	2.10	1085
Hexyl acetate				0.810	2.70	1100	0.775	3.60	1158	0.620	3.88	1219
Octyl acetate				2.200	7.96	1313				1.49	9.31	1438
Methyl propionate	0.155	0.235	607	0.120	0.390	716	0.105	0.512	764	0.114	0.76	836
Ethyl propionate	0.220	0.335	679	0.165	0.550	784	0.140	0.700	829	0.150	1.00	900
Propyl propionate	0.375	0.570	787	0.290	0.950	890	0.255	1.18	933	0.230	1.55	1006
Isopropyl propionate	0.265	0.405	717	0.210	0.700	832	0.165	0.770	847	0.190	1.19	941
Butyl propionate	0.630	0.955	891	0.460	1.53	981	0.410	1.95	1035	0.390	2.44	1110
2-Methylpropyl propionate	0.520	0.790	853	0.380	1.26	948	0.310	1.50	983	0.305	2.00	1060
Pentyl propionate	1.060	1.602	998	0.770	2.56	1092	0.685	3.14	1132	0.600	3.75	1210
3-Methylbutyl propionate	0.860	1.304	955	0.620	2.07	1043	0.550	2.50	1086	0.472	3.15	1170
Hexyl propionate				1.250	4.16	1184	1.085	5.05	1228	0.930	5.82	1314
Octyl propionate							2.785	12.95	1420	2.32	14.50	1524

Methyl butyrate	0.260	0.397	714	0.190	0.630	811	0.170	0.78	850	0.170	1.13	930
Ethyl butyrate	0.375	0.565	788	0.260	0.930	887	0.225	1.07	914	0.230	1.44	988
Propyl butyrate	0.605	0.920	884	0.440	1.57	987	0.395	1.80	1018	0.360	2.25	1090
Isopropyl butyrate	0.450	0.680	823	0.320	1.07	915	0.255	1.19	933	0.250	1.66	1026
Butyl butyrate	0.975	1.48	980	0.690	2.47	1081	0.645	2.93	1117	0.535	3.35	1188
2-Methylpropyl butyrate	0.780	1.18	937	0.590	1.97	1036	0.470	2.35	1073	0.435	2.72	1131
Pentyl butyrate	1.550	2.35	1075	1.150	4.11	1182	1.030	4.78	1215	0.820	5.12	1283
3-Methylbutyl butyrate	1.300	1.97	1039	0.995	3.32	1140	0.835	3.80	1171	0.685	4.28	1236
Hexyl butyrate				2.07	6.704	1281	1.630	7.58	1311	1.255	7.80	1381
Octyl butyrate				5.05	18.10	1475	4.135	19.20	1494	2.94	18.37	1576
Methyl isobutyrate	0.210	0.319	669									
Ethyl isobutyrate	0.295	0.445	738	0.213	0.710	838	0.175	0.83	865	0.160	1.19	941
Propyl isobutyrate	0.475	0.722	836	0.340	1.130	926	0.280	1.40	970	0.270	1.69	1028
Isopropyl isobutyrate	0.370	0.565	785	0.240	0.770	850	0.185	0.86	868	0.185	1.23	952
Butyl isobutyrate	0.770	1.17	933	0.550	1.83	1024	0.475	2.21	1060	0.615	2.80	1141
2-Methylpropyl isobutyrate	0.660	0.997	900	0.460	1.490	980	0.380	1.73	1010	0.360	2.25	1090
Pentyl isobutyrate	1.265	1.87	1032	0.930	3.10	1125	0.780	3.54	1152	0.660	4.10	1244
3-Methylbutyl isobutyrate	1.050	1.59	998	0.760	2.46	1080	0.615	2.86	1108	0.550	3.44	1192
Hexyl isobutyrate				1.482	4.94	1220	1.225	5.70	1250	1.050	6.57	1341
Octyl isobutyrate				4.110	13.28	1416	3.125	14.55	1443	2.325	15.50	1541
Methyl pentanoate	0.430	0.650	814	0.290	1.07	915	0.300	1.40	970	0.300	2.00	1060
Ethyl pentanoate	0.595	0.900	879	0.450	1.50	978	0.410	1.90	1029	0.370	2.31	1100
Propyl pentanoate	0.975	1.480	980	0.760	2.46	1080	0.645	3.00	1126	0.580	3.63	1205
Isopropyl pentanoate	0.725	1.110	921	0.505	1.68	1003	0.430	2.00	1040	0.400	2.50	1118
Butyl pentanoate	1.545	2.34	1074	1.240	4.01	1178	1.070	4.86	1218	0.850	5.67	1304
2-Methylpropyl pentanoate	1.300	1.97	1027	0.990	3.30	1138	0.785	3.74	1166	0.710	4.44	1251
Pentyl pentanoate	2.455	3.72	1170	1.850	6.40	1270	1.615	7.50	1312	1.260	8.40	1395
3-Methylbutyl pentanoate	2.060	3.12	1134	1.585	5.28	1232	1.335	6.21	1268	1.00	6.65	1344
Hexyl pentanoate				3.06	10.20	1360	2.555	12.0	1404	1.870	12.46	1491
Octyl pentanoate							6.315	29.8	1589	4.230	28.15	1679

(continued on p. 414)

TABLE II (continued)

Ester	Stationary phase														
	SE-30				OV-17				OV-25				XE-60		
	$V_g(a)$	$V_R(b)$	I_R	$V_g(a)$	$V_R(b)$	I_R	$V_g(a)$	$V_R(b)$	I_R	$V_g(a)$	$V_R(b)$	I_R	$V_g(a)$	$V_R(b)$	I_R
Methyl 3-methylbutyrate	0.325	0.508	764	0.270	0.900	880	0.235	1.10	915	0.215	1.41	982	0.215	1.41	982
Ethyl 3-methylbutyrate	0.490	0.740	840	0.339	1.130	926	0.315	1.44	972	0.275	1.72	1029	0.275	1.72	1029
Propyl 3-methylbutyrate	0.785	1.19	937	0.570	1.900	1028	0.490	2.25	1063	0.420	2.62	1126	0.420	2.62	1126
Isopropyl 3-methylbutyrate	0.605	0.92	883	0.370	1.230	943	0.320	1.49	976	0.305	1.91	1053	0.305	1.91	1053
Butyl 3-methylbutyrate	1.250	1.89	1030	0.920	3.06	1128	0.780	3.58	1156	0.630	4.05	1225	0.630	4.05	1225
2-Methylpropyl 3-methylbutyrate	1.040	1.58	994	0.730	2.43	1073	0.585	2.86	1108	0.520	3.25	1179	0.520	3.25	1179
Pentyl 3-methylbutyrate	1.975	2.99	1125	1.650	5.30	1230	1.145	5.45	1243	0.980	6.12	1320	0.980	6.12	1320
3-Methylbutyl 3-methylbutyrate	1.665	2.52	1088	—	3.95	1175	1.040	4.70	1200	0.795	4.96	1276	0.795	4.96	1276
Hexyl 3-methylbutyrate	—	—	—	2.590	8.35	1320	1.920	9.14	1345	1.465	9.16	1418	1.465	9.16	1418
Octyl 3-methylbutyrate	—	—	—	—	—	—	—	—	—	3.425	21.42	1616	3.425	21.42	1616
Methyl hexanoate	0.700	1.06	913	0.550	1.83	1024	0.490	2.25	1063	0.434	2.70	1130	0.434	2.70	1130
Ethyl hexanoate	0.970	1.47	980	0.750	2.68	1100	0.645	3.08	1128	0.520	3.26	1179	0.520	3.26	1179
Propyl hexanoate	1.560	2.36	1077	1.390	4.35	1196	1.065	4.90	1219	0.830	5.19	1286	0.830	5.19	1286
Isopropyl hexanoate	1.175	1.78	1018	0.920	3.07	1123	0.725	3.30	1143	0.580	3.63	1205	0.580	3.63	1205
Butyl hexanoate	2.475	3.75	1170	2.340	7.30	1296	1.665	7.64	1310	1.260	7.88	1382	1.260	7.88	1382
2-Methylpropyl hexanoate	2.035	3.08	1131	1.695	5.65	1245	1.315	6.02	1258	1.040	6.51	1339	1.040	6.51	1339
Pentyl hexanoate	3.940	5.96	1268	3.630	11.72	1392	2.645	12.12	1406	1.960	12.20	1482	1.960	12.20	1482
3-Methylbutyl hexanoate	3.250	4.93	1227	2.755	9.18	1342	2.020	9.52	1357	1.565	9.79	1433	1.565	9.79	1433
Hexyl hexanoate	—	—	—	—	—	—	4.225	19.68	1508	2.720	18.09	1577	2.720	18.09	1577
Octyl hexanoate	—	—	—	—	—	—	—	—	—	6.220	41.40	1766	6.220	41.40	1766
Methyl 4-methylpentanoate	0.580	0.88	876	0.500	1.65	1000	0.395	1.84	1020	0.355	2.25	1090	0.355	2.25	1090
Ethyl 4-methylpentanoate	0.825	1.25	947	0.648	2.16	1051	0.550	2.56	1090	0.455	2.84	1142	0.455	2.84	1142
Propyl 4-methylpentanoate	1.295	1.96	1038	1.050	3.50	1152	0.850	3.96	1180	0.700	4.38	1244	0.700	4.38	1244
Isopropyl 4-methylpentanoate	0.995	1.51	985	0.770	2.49	1082	0.585	2.66	1095	0.517	3.20	1173	0.517	3.20	1173
Butyl 4-methylpentanoate	2.105	3.20	1138	1.655	5.52	1246	1.400	6.37	1270	1.060	6.63	1344	1.060	6.63	1344
2-Methylpropyl 4-methylpentanoate	1.750	2.65	1100	1.500	4.70	1210	1.055	4.80	1220	0.855	5.35	1294	0.855	5.35	1294
Pentyl 4-methylpentanoate	3.315	5.02	1232	3.080	9.45	1350	2.185	10.00	1360	1.615	10.10	1441	1.615	10.10	1441
3-Methylbutyl 4-methylpentanoate	2.805	4.25	1198	2.470	7.70	1308	1.635	7.79	1316	1.380	8.03	1391	1.380	8.03	1391
Hexyl 4-methylpentanoate	—	—	—	3.975	13.25	1415	3.435	15.80	1466	2.450	15.30	1540	2.450	15.30	1540
Octyl 4-methylpentanoate	—	—	—	—	—	—	8.735	40.60	1650	5.625	35.20	1734	5.625	35.20	1734

parallel plots as did the butyrate, pentanoate and hexanoate esters, but of slightly lower slope. A different behaviour is observed with XE-60, where the slopes are all very similar but with the propionate esters having a slightly greater slope than the other ester series.

When the number of carbon atoms in the acid chain was three or more, an incremental increase in the carbon number in either the acid or alcohol chain resulted in an increase of 95, 97, 96 and 100 retention index units per methylene group using the stationary phases SE-30, OV-17, OV-25 and XE-60, respectively. With the alkyl formates on SE-30 an increase of about 108 retention index units per methylene group in the alcohol chain was observed while on the other phases the differences in slope of the formate and other ester lines were lower and the differences in retention indices were accordingly less.

The increased and decreased retention of the methyl and isopropyl esters on the four phases are shown in Table III.

TABLE III

RETENTION INDEX VARIATION FOR METHYL AND ISOPROPYL ESTERS

Esters	Stationary phase			
	SE-30	OV-17	OV-25	XE-60
Methyl	30	35	30-40	25-50
Isopropyl	20	25	25-35 ^a	15-30

^a Isopropyl formate exhibited a decreased retention of nearly 50 index units

The relative retention of the various esters when plotted against the number of carbon atoms in the acid chain (R) produced a series of essentially linear relationships on the various stationary phases. The plots for esters on the OV-25 and XE-60 phases are shown in Fig. 2.

The normal esters where R = 4, 5 and 6 produced parallel plots while esters where R = 0 to 3 showed a gradual decrease in slope from R = 0 to R = 3.

Plots of this type have been shown¹ to accentuate the difference in retention behaviour of methyl formate and the other methyl esters on SE-30. The same effect is apparent with the OV-17 and OV-25 phases but with XE-60 the reverse behaviour occurs, *i.e.* methyl formate and the other methyl esters produce a linear relationship while the formates in the other plots show an increased retention in Figs. 2a and b. The difference is shown in Figs. 2a and b, with results on OV-25 and XE-60 stationary phases. With chromatography on the XE-60 stationary phase and to a lesser extent on OV-25 it was apparent that the fit of the points to the various plots was not as satisfactory as with SE-30 and OV-17 or with the α -alkylacrylic esters on the SE-30 stationary phase where linear plots with the acid carbon chain (R) as an ordinate were first reported⁴. Further studies are being undertaken using polysiloxane stationary phase with Rohrschneider constants intermediate between OV-25 and XE-60 and greater than XE-60 using both aliphatic and olefinic esters such that the applicability of the relationship shown in Fig. 2 can be more widely examined.

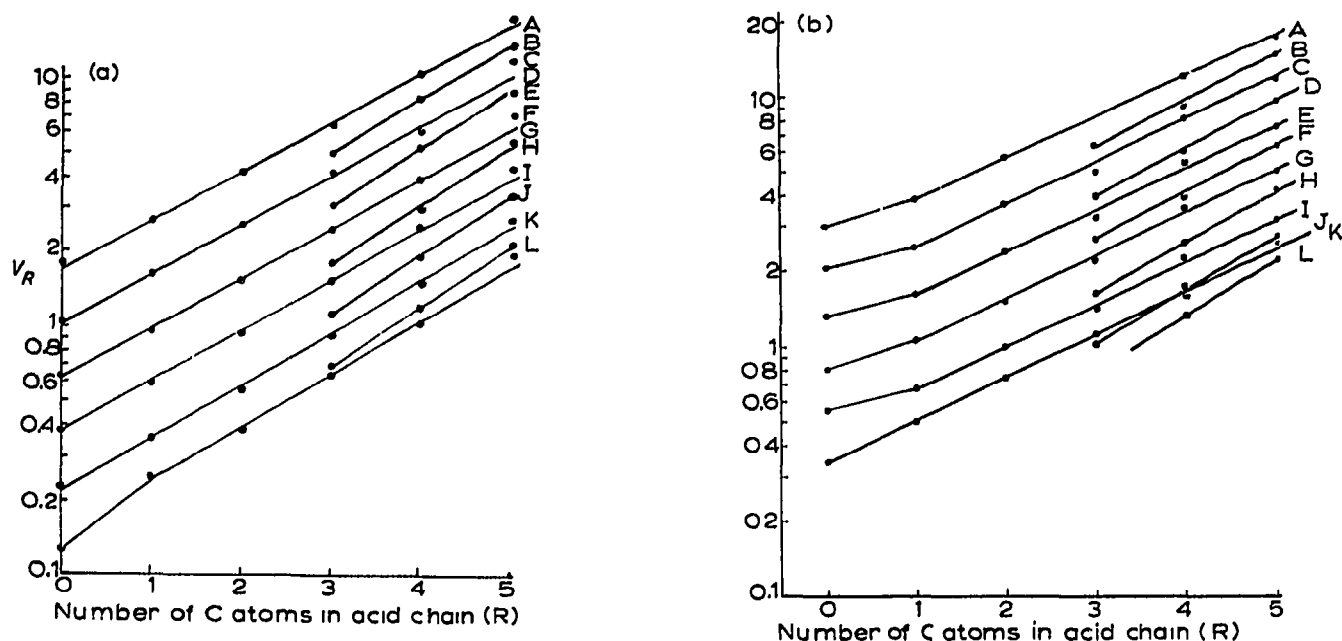


Fig 2. Plots of the logarithm of the relative retention volume *versus* the number of carbon atoms in the acid chain of saturated esters on (a) OV-25 and (b) XE-60 stationary phases with R of both normal and isostructure while the alcohol chain is linear.

A = $\text{RCOOC}_6\text{H}_{13}$; B = $\text{isoRCOOC}_6\text{H}_{13}$; C = $\text{RCOOC}_5\text{H}_{11}$;
 D = $\text{isoRCOOC}_5\text{H}_{11}$; E = RCOOC_4H_9 ; F = $\text{isoRCOOC}_4\text{H}_9$;
 G = RCOOC_3H_7 ; H = $\text{isoRCOOC}_3\text{H}_7$; I = RCOOC_2H_5 ;
 J = $\text{isoRCOOC}_2\text{H}_5$; K = RCOOCH_3 ; L = isoRCOOCH_3 .

It has been shown with SE-30 that normal and isoesters having the same carbon number in the acid chain (R) exhibit a constant decrease in retention index, but the decrease varies for esters of different acid chain length¹. A similar situation exists with chromatography on the other phases and the incremental decreases for the various ester series on each phase is shown in Table IV.

No worthwhile conclusion can be drawn from this comparison. It is evident, however, that the earlier observation¹ that as the number of carbon atoms in the acid chain increases, the decrease in retention due to branching in the acid chain is reduced, is not generally apparent.

The effect of branching in the alkyl groups on both sides of the carbonyl group are shown in Figs. 3 and 4.

TABLE IV

RETENTION INDEX DECREASES ON BRANCHING IN THE ACID CHAIN

Carbon number in acid chain R	Stationary phase			
	SE-30	OV-17	OV-25	XE-60
3	47	59	55	45
4	43	47	60	75
5	35	49	41	39

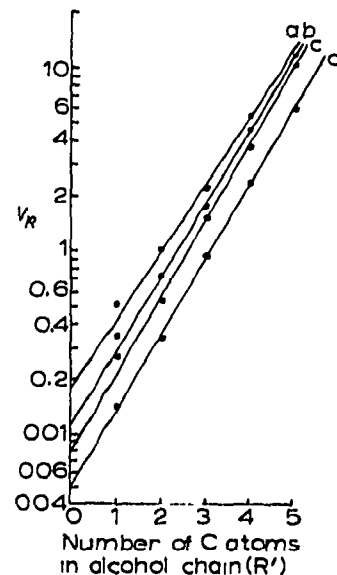
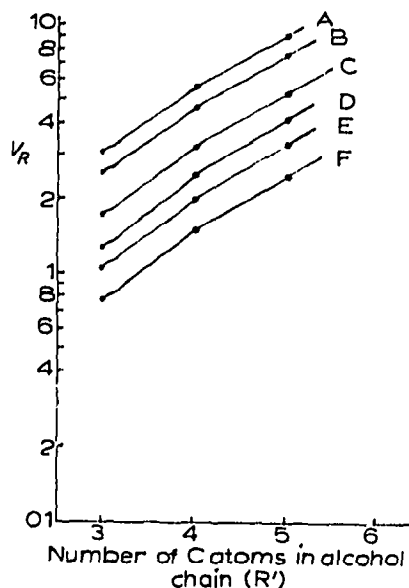


Fig. 3. Plots of logarithm of relative retention *versus* number of carbon atom in the alcohol chain of saturated esters on OV-17 stationary phase with isoalcohol chains (R') and with normal and isoacid chains.

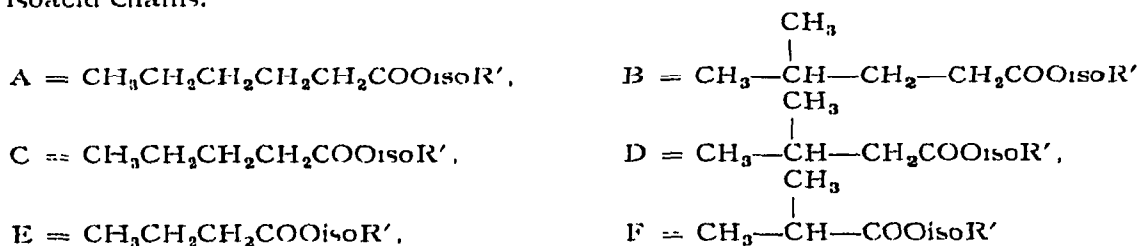


Fig. 4. Plots of logarithm of relative retention *versus* number of carbon atoms in the alcohol chain of normal saturated esters where $R = R'$ on (a) SE-30, (b) OV-17, (c) OV-25 and (d) XE-60 stationary phases

Plots of relative retention for the isoalkyl esters with respect to the isoalkyl branched acid chain esters are shown in Fig. 3 for the OV-17 phase and it is evident that branching of the acid chain reduces the retention of the isoalkyl esters by a constant factor for esters with a constant number of carbon atoms in the acid chain. The retention index differences for the four phases are shown in Table V.

The effect of the carboxyl group on the retention of the n -alkyl esters is apparent from Fig. 4. An essentially linear relationship for esters with the same number

TABLE V

EFFECT OF BRANCHING OF ISOALKYL ESTERS

Acid chain length	Stationary phase			
	SE-30	OV-17	OV-25	XE-60
3	40	60	63	57
4	46	59	64	52
5	30	35	48	46

of carbon atoms in the R and R' chains is achieved and a constant effect of the carboxyl group by both R and R' is indicated.

By extrapolation of the plot to zero, *i.e.* $R = R' = 0$, the net retention volume of the carboxyl group was obtained. The net retention of the group increased with increasing polar character of the column and is approximately 304, 410, 450 and 520 retention index units for the SE-30, OV-17, OV-25 and XE-60 stationary phases, respectively.

Examination of the actual retention characteristics on the four stationary phases shows that relative retention volumes on less polar phases are smaller. The retention volume of the hydrocarbon reference compounds decreases with increasing polar character of the column such that esters on the XE-60 phase had the smallest denominator and thereby the highest V_R and I_R , the net retention being highest on the least polar phase.

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