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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS*

PART I. SIMPLE ALIPHATIC ESTERS

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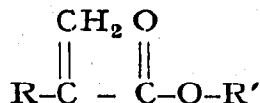
SUMMARY

The retention behaviour of a number of series of homologous esters on a non-polar stationary phase is reported together with correlations that are possible due to the structure of the compounds. The influence of the boiling point on retention is shown and the anomalous behaviour of methyl and isopropyl esters is considered.

INTRODUCTION

Certain compounds may on account of their structure be considered as members of two or more homologous series. In these cases correlation between retention behaviour and the individual structural parameters is possible. Evaluation of the retention data of such series may be carried out in several ways, *viz.* (a) by use of a series of graphical plots as have been extensively employed with fatty esters^{1,2}; (b) by construction of a nomograph from the experimental data; or (c) by examination of the incremental increases in the retention indices of the series of compounds.

Studies were made of the homologous series of the α -alkylacrylic esters represented by the formula:



where R and R' are both alkyl groups with values of 0 to 6 and 1 to 6, respectively³. With one alkyl group constant, the other was used with varying carbon number to produce a logarithmic relationship with retention data. By plotting a number of series of compounds where R and R' are varied a set of plots in the form of a network was produced. Nomographic representation of the experimentally obtained data was also reported and it was observed that an increase in the alkyl carbon chain (R') had

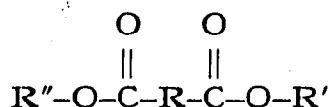
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a greater effect on the retention than a corresponding increase in the α -alkyl carbon chain (R).

Incremental increases in retention indices have been reported for some homologous esters by WEHRLI AND KOVATS⁴, where an increase of 100 index units per ester homologue containing five or more carbon atoms was reported. A later publication⁵ states: "In any homologous series the retention index of the higher members increases by 100 index units per CH₂ group introduced", this implying that the slopes of conventional retention data plots of all homologous series of compounds are the same. ZULAICA AND GUIOCHON⁶ have studied aliphatic dibasic esters (*i.e.* oxalates, succinates, adipates, suberates, sebacates) and aromatic esters (phthalates).

Aliphatic dibasic esters may be represented as



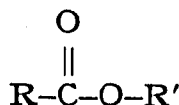
and it has been shown that the retention index contribution of a methylene group in R and R' or R'' is not equivalent, R having a value approximating 100 while R' and R'' have values of 90-95. With phthalates the value for R' and R'' is less than 90.

Gas chromatography of aliphatic esters has been reported by a variety of workers⁷, but the most extensive studies relevant to this work are those of WEHRLI AND KOVATS⁴ and of REYNOLDS⁸, and where they are comparable satisfactory agreement is observed with the present work.

SCHOMBURG⁹ has reported retention indices for a large number of methyl esters of isomeric aliphatic monocarboxylic acids using a capillary column with squalane as a non-polar stationary phase. The relationship between retention data and chemical structure has been discussed together with the effect of varying polarity by the use of propylene glycol and propylene glycol sebacate as stationary phases.

Linear relationships were shown between retention indices and boiling point of the normal and branched-chain methyl esters, the latter plot having the lower slope. The equations of the two plots were determined and empirical relationships reported which allowed calculation of retention index or boiling point of the appropriate ester under the experimental conditions used.

In this work the behaviour of a number of homologous series of aliphatic esters is reported. The esters are represented as:



where the carbon number of the acid (R) and alcohol (R') chains varied between 0 and 5 and 1 and 5, respectively, with both normal and branched-chain homologues being considered.

The influence of the boiling point on the retention of the esters on a non-polar stationary phase is reported and it is apparent that with little hydrogen bonding occurring the retention behaviour is primarily related to the boiling point of the esters. The common deviation of the retention of methyl esters from a linear relation-

ship with carbon number and a similar effect with isopropyl esters is primarily due to their generally markedly higher boiling points with respect to the other esters of the homologous series rather than to any column effect.

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.

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 packed with 10% Methyl Silicone Polymer SE-30 on 60-80 mesh acid-washed and silanised Celite 560 were used 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.

In order that variations in the operating conditions would not affect the results the esters were examined at random according to a table of random digits. When the operating conditions were achieved a mixture of alkanes (C_5 to C_{13}) were chromatographed and from these data the retention times of the esters were determined as retention indices.

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

TABLE I

RETENTION DATA FOR ALIPHATIC ESTERS

<i>Ester</i>	V_g^a	V_R^b	I_R
Methyl formate	0.050	0.075	380
Ethyl formate	0.085	0.129	487
Propyl formate	0.145	0.216	592
Isopropyl formate	0.105	0.162	528
Butyl formate	0.250	0.375	703
2-Methylpropyl formate	0.200	0.301	660
Pentyl formate	0.425	0.645	812
3-Methylbutyl formate	0.350	0.512	774
Methyl acetate	0.093	0.140	506
Ethyl acetate	0.130	0.200	571
Propyl acetate	0.225	0.338	683
Isopropyl acetate	0.170	0.259	625
Butyl acetate	0.375	0.585	787
2-Methylpropyl acetate	0.310	0.468	750
Pentyl acetate	0.645	0.980	898
3-Methylbutyl acetate	0.525	0.798	854
Methyl propionate	0.155	0.235	607
Ethyl propionate	0.220	0.335	679
Propyl propionate	0.375	0.570	787
Isopropyl propionate	0.265	0.405	717

(continued on p. 36)

TABLE 1 (Continued)

Ester	V_R^a	V_R^b	I_R
Butyl propionate	0.630	0.955	891
2-Methylpropyl propionate	0.520	0.790	853
Pentyl propionate	1.060	1.602	998
3-Methylbutyl propionate	0.860	1.304	955
Methyl butyrate	0.260	0.397	714
Ethyl butyrate	0.375	0.565	788
Propyl butyrate	0.605	0.920	884
Isopropyl butyrate	0.450	0.680	823
Butyl butyrate	0.975	1.48	980
2-Methylpropyl butyrate	0.780	1.18	937
Pentyl butyrate	1.550	2.35	1075
3-Methylbutyl butyrate	1.300	1.97	1039
Methyl isobutyrate	0.210	0.319	669
Ethyl isobutyrate	0.295	0.445	738
Propyl isobutyrate	0.475	0.722	836
Isopropyl isobutyrate	0.370	0.565	785
Butyl isobutyrate	0.770	1.17	933
2-Methylpropyl isobutyrate	0.660	0.997	900
Pentyl isobutyrate	1.265	1.87	1032
3-Methylbutyl isobutyrate	1.050	1.59	998
Methyl valerate	0.430	0.650	814
Ethyl valerate	0.595	0.900	879
Propyl valerate	0.975	1.48	980
Isopropyl valerate	0.725	1.11	921
Butyl valerate	1.545	2.34	1074
2-Methylpropyl valerate	1.300	1.97	1027
Pentyl valerate	2.455	3.72	1170
3-Methylbutyl valerate	2.060	3.12	1134
Methyl 3-methylbutyrate	0.335	0.508	764
Ethyl 3-methylbutyrate	0.490	0.740	840
Propyl 3-methylbutyrate	0.785	1.19	937
Isopropyl 3-methylbutyrate	0.605	0.92	883
Butyl 3-methylbutyrate	1.250	1.89	1030
2-Methylpropyl 3-methylbutyrate	1.040	1.58	994
Pentyl 3-methylbutyrate	1.975	2.99	1125
3-Methylbutyl 3-methylbutyrate	1.665	2.52	1088
Methyl hexanoate	0.700	1.06	913
Ethyl hexanoate	0.970	1.47	980
Propyl hexanoate	1.560	2.36	1077
Isopropyl hexanoate	1.175	1.78	1018
Butyl hexanoate	2.475	3.75	1170
2-Methylpropyl hexanoate	2.035	3.08	1131
Pentyl hexanoate	3.940	5.96	1268
3-Methylbutyl hexanoate	3.250	4.93	1227
Methyl 4-methylpentanoate	0.580	0.88	876
Ethyl 4-methylpentanoate	0.825	1.25	947
Propyl 4-methylpentanoate	1.295	1.96	1038
Isopropyl 4-methylpentanoate	0.995	1.51	985
Butyl 4-methylpentanoate	2.105	3.20	1138
2-Methylpropyl 4-methylpentanoate	1.750	2.65	1100
Pentyl 4-methylpentanoate	3.315	5.02	1232
3-Methylbutyl 4-methylpentanoate	2.805	4.25	1198

^a Corrected for dead volume.

^b Relative to nonane.

DISCUSSION OF RESULTS

A plot of the logarithm of the relative retention *versus* the number of carbon

atoms in the alcohol chain (R') for the normal and isoester series is shown in Fig. 1. With a constant number of carbon numbers in the acid chain (R), log retention for esters with two or more carbon atoms in the alcohol chain increases linearly with an increase in the number of carbon atoms. From Fig. 1 it is apparent that the isopropyl esters and methyl esters with the exception of methyl formate deviated from linearity.

The slopes of all the plots decrease as the number of carbon atoms in the acid

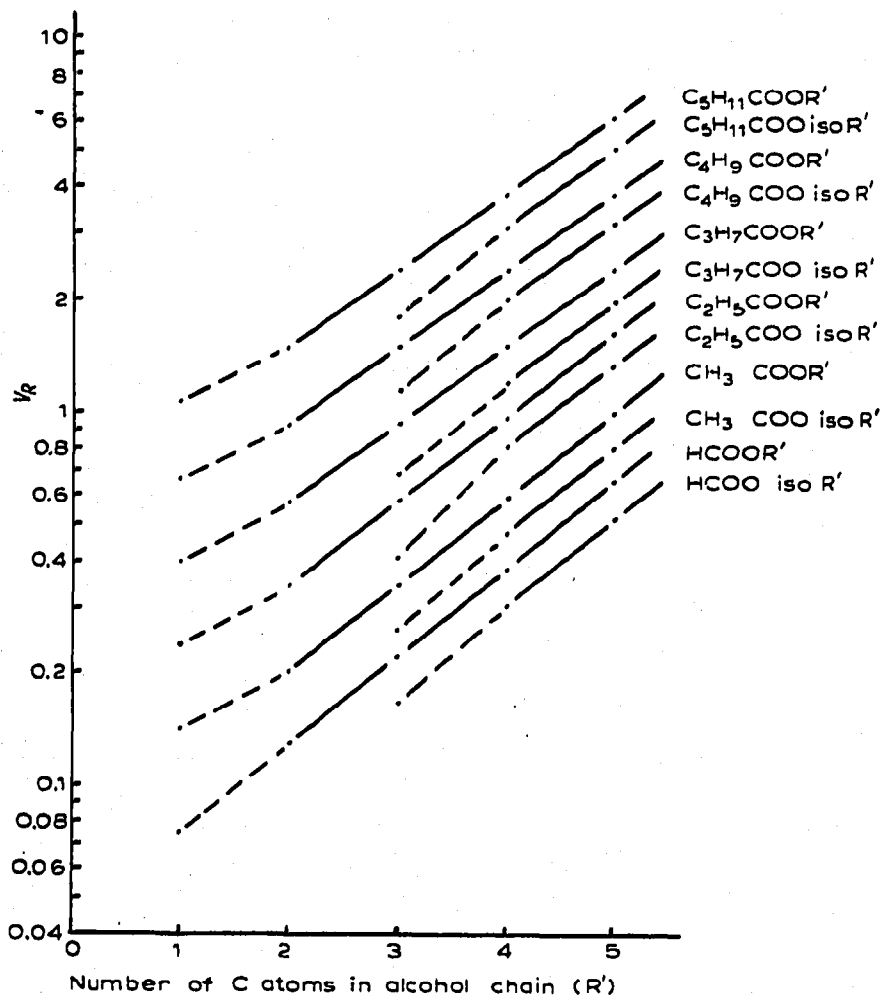


Fig. 1. Plots of logarithm of relative retention *versus* number of carbon atoms in alcohol chain of saturated esters with varying alcohol chain (R') length with R' forming both normal and isoesters while the acid chain (R) is linear.

chain is increased, *i.e.* from R equals 0 to 3, after which the plots are parallel, *i.e.* butyrates, valerates and hexanoates.

The retention indices are shown in Table I and it is apparent that when the number of carbon atoms in the acid chain is 3 or more, an incremental increase in carbon number in either the acid or alcohol chain will result in an increase of approximately 95 units per methylene group, while with the alkyl formates an increase in retention index of about 108 units per methylene group in the alcohol chain was

observed. With the methyl esters the increased retention was found to be about 30 units.

Replacement of the normal alcohols by the branched-chain isomers resulted in a decrease in retention index of approximately 60 units for the isopropyl esters and approximately 40 units for the isobutyl and isopentyl esters.

The relative retention of the various esters plotted against the number of carbon atoms in the acid chain (R) is shown in Fig. 2 and it is apparent that a series of linear relationships exists, the plots of the normal esters being similar to those shown previously with α -alkylacrylic esters³. The slopes of the plots representing esters with a constant number of carbon atoms in the alcohol chain (R') are almost parallel, but

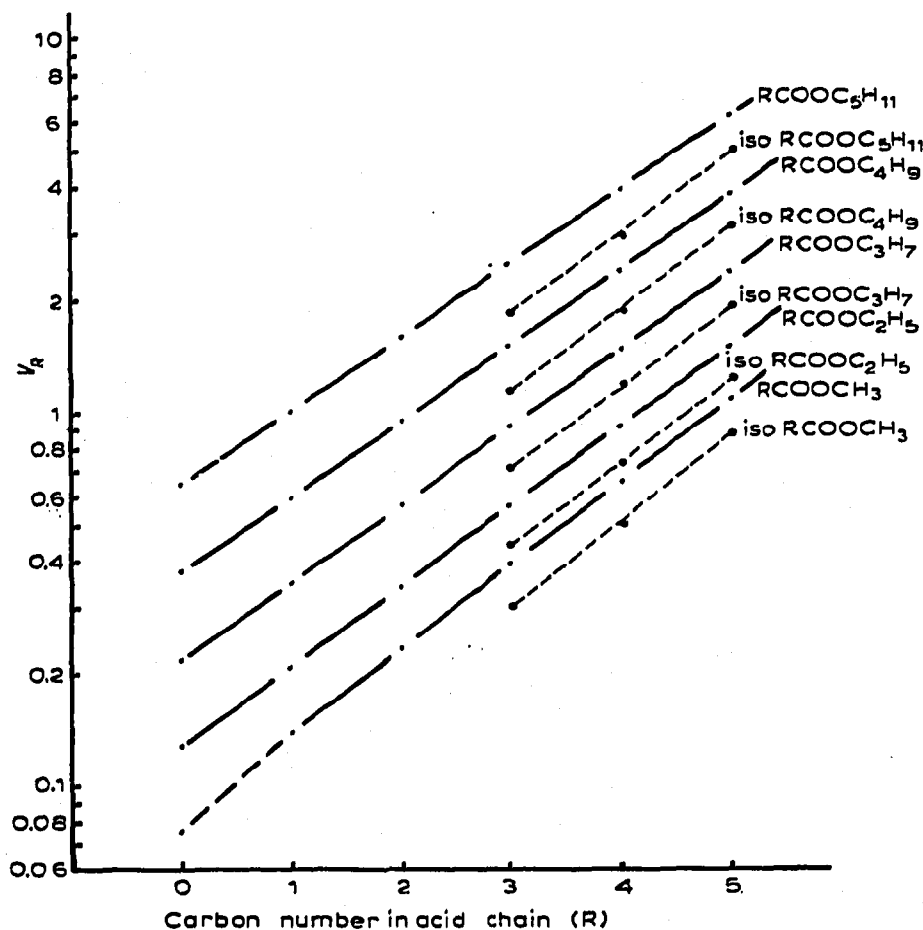


Fig. 2. Plots of logarithm of relative retention *versus* number of carbon atoms in the acid chain (R) with R of both normal and iso-structure while the alcohol chain is linear.

there is a very gradual decrease in slope as the number of carbon atoms in the alcohol chain is increased. The plot accentuates the difference in retention behaviour of methyl formate and the other methyl esters.

From Table II where the retention indices of the normal and isoesters are compared it is apparent that esters having the same carbon number in the acid chain (R) exhibit a constant decrease in retention, but this decrease varies for esters having

TABLE II

EFFECT OF BRANCHING IN ACID CHAIN ON RETENTION BEHAVIOUR OF *n*-ALKYL ESTERS

Carbon number in acid chain (R)	Carbon number in alcohol chain (R')	Carbon number in alcohol chain (R')				
		1	2	3	4	5
3	<i>n</i>	714	788	884	980	1075
	<i>iso</i>	669	738	836	933	1032
		45	50	48	47	45
4	<i>n</i>	814	879	980	1074	1170
	<i>iso</i>	764	840	937	1030	1125
		50	39	43	44	45
5	<i>n</i>	913	980	1077	1170	1268
	<i>iso</i>	876	947	1038	1138	1232
		37	33	39	32	36

different acid chain lengths. The decreases in I_R for the isobutyrate, isovalerate and isohexanoate were 47, 43 and 35 index units, respectively. Thus from Fig. 2 and Table II it is evident 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.

The effect of branching in both the acid and alcohol chains is shown in Figs. 3,

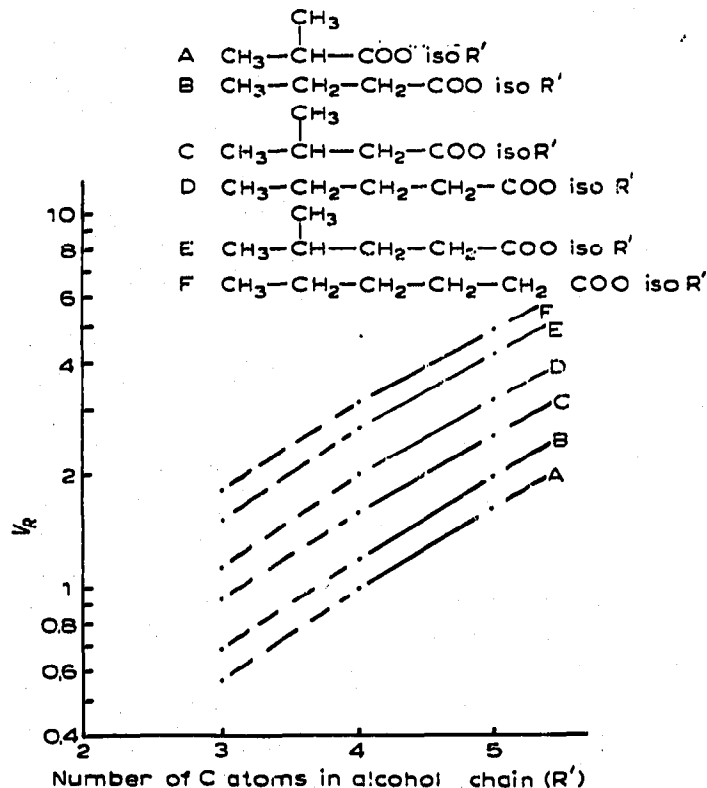


Fig. 3. Plots of logarithm of relative retention of saturated esters with isoalcohol (R') chains and with normal and isoacid chains.

4 and 5, where the straight-chain alkyl groups in both R and R' are replaced by the appropriate branched-chain groups.

Fig. 3 shows plots of relative retention for the isoalkyl esters with respect to the isoalkyl branched acid chain esters and it is apparent that branching of the acid chain further 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 amount by which branching in the acid chain reduced the retention of the isoalkyl esters was found to be approximately 40, 46 and 30 index units for the isobutyrate, isovalerate and isohexanoate, respectively. In common with the normal esters the reduction in retention due to branching in the acid chain tended to decrease as the number of carbon atoms in the acid chain increased.

Fig. 4 shows the influence of branching in the alcohol chain when the acid chain is branched. The logarithm of retention for the isobutyl and isopentyl esters with a constant value of R were lower than for the normal esters by a constant factor, while the reduction with the isopropyl esters was greater than with the isobutyl and isopentyl esters. From the retention indices of these esters it is observed that the reduction in retention due to branching in the alcohol chain is less for the *n*-alkyl isoesters than for the corresponding *n*-alkyl esters. The isobutyl and isopentyl isoesters had retention indices 35 units less than the corresponding *n*-butyl and *n*-pentyl isoesters as compared to a reduction of 40 units when branching was

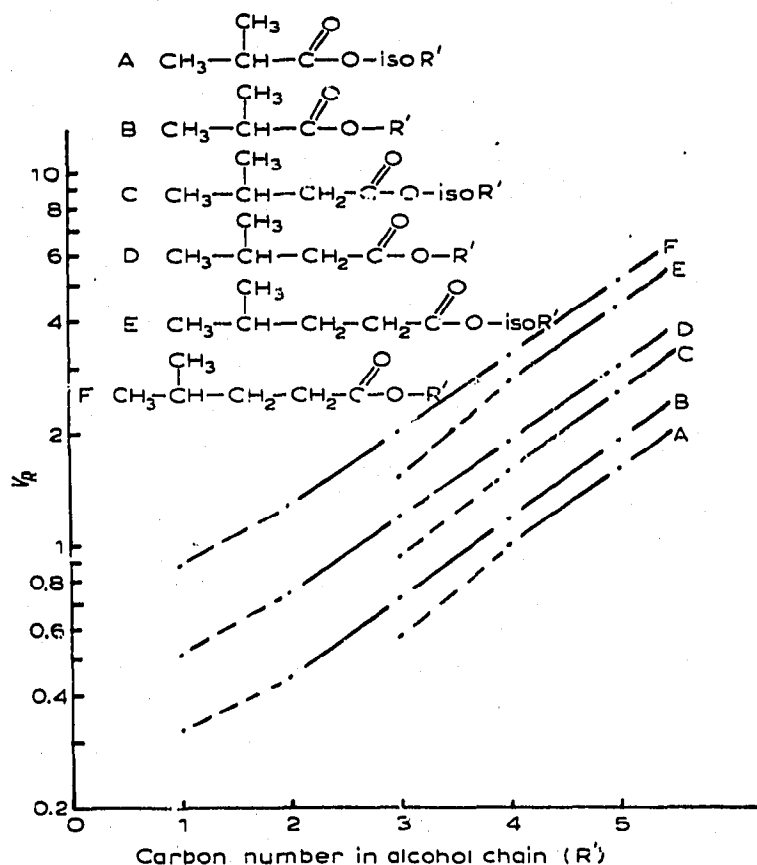


Fig. 4. Plots of logarithm of relative retention of saturated esters with isoacid (R) chains and with normal and isoalcohol chains.

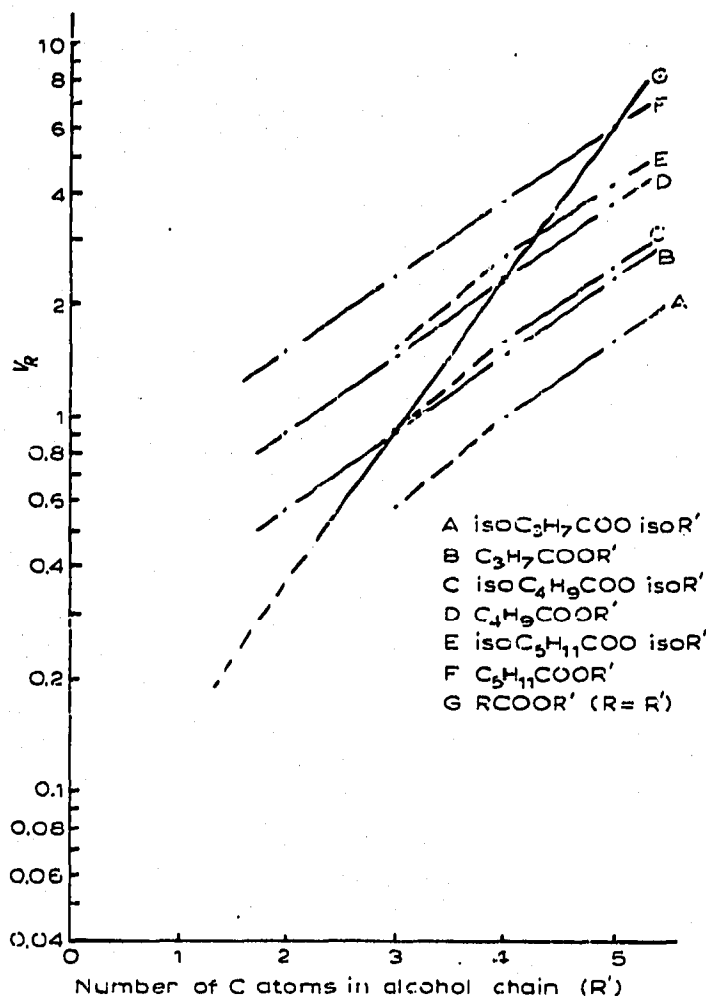


Fig. 5. Plots of logarithm of relative retention of saturated esters with varying alcohol carbon chain (R') and where both alkyl chains are either branched or straight.

introduced into the alcohol chain of the straight acid chain esters. With the isopropyl isoesters branching in the alcohol chain produced a reduction of about 53 units.

The effect of branching in both R and R' chains is shown in Fig. 5, where plots of the esters with either straight-chain or branched-chain R and R' are parallel. It is apparent that with branching in both R and R' the total reduction in retention due to the branched-chain structure is decreased as the length of the acid chain (R) is increased. This is due to the reduction of retention caused by branching in the acid chain (R) with increasing acid chain length as observed earlier.

The difference in the retention indices of the *n*-propyl and the isopropyl isoesters varies between 90 and 100 units, while with the isobutyl and isopentyl series a decrease of 70 to 80 units is observed.

The effect of the carboxyl group on the retention of the *n*-alkyl esters is apparent from Fig. 5. A linear relationship for esters with the same number of carbon atoms in R and R' and retention is apparent and a constant effect on the carboxyl group by both R and R' is indicated.

By extrapolation of the plot to zero, *i.e.* R and R' equal zero, the net retention

volume of the carboxyl group was found and by conversion to retention indices, retention of the carboxyl group was found to be 304 index units. This is in good agreement with the value of 290 units reported by ZULAICA AND GUIOCHON⁶ for dibasic esters using an SE-30 stationary phase at a temperature of 220° and a carrier gas flow rate of 200 ml/min.

The retention values of the carboxyl group for the systems where the esters have either R or R' or both of them as branched chains may be similarly established, however, the data in the present work (*i.e.* two reliable points) are inadequate.

The relationships between boiling point and carbon number¹⁰ and between chromatographic retention and boiling point¹¹ of homologous series are well known. When the data of the esters presented here are considered with regard to boiling point the following features common to retention behaviour are apparent:

(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.

(2) The methyl esters have slightly higher boiling points than expected from the slope 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 slope of 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.

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