
Capillary Gas Chromatography of Esters

Correlations between Structure and Retention Index

F. Saura Calixto / A. García Raso

Department of Organic Chemistry, Science Faculty, The University of Palma de Mallorca, Spain

Key Words

Capillary columns
Gas chromatography
Retention index
Structure

Summary

The retention index of twenty different homologous series of esters have been determined experimentally on polar (Carbowax 1540) and non-polar (squalane) columns. General equations to calculate retention index have been established by statistical methods. The influence of the length and inductive effect of acid and alcohol chains and the relative position of the carboxylic group are discussed.

Introduction

Many papers have been published that relate the molecular structure of different compounds to their retention indices. In some cases these indices, determined by experimental means, are compared with those empirically deduced from their atomic and molecular properties [1–4].

Other authors have studied retention indices for homologous series in order to establish correlations with their structure. Increases of index corresponding to the methylene group, polarity of stationary phases and comparisons of isomers have been studied. Papers of this kind, such as those of Sojak et al. [5–7] and Rang et al. [8, 9] with alkylbenzenes and alkynes, have usually been concerned with different types of hydrocarbons.

Studies of the behaviour of esters using gas chromatographic methods, however, are not very numerous [10, 11]. These compounds are constituents of the volatile component of fruits and other foods.

In our case, in order to carry out a full analytical study of volatile fruit components [12–14], we have determined retention indices experimentally on some one hundred esters in two stationary phases in capillary columns (Carbo-

wax 1540 and squalane) at different temperatures. We can group these esters in twenty different homologous series. From a comparative study of the retention indices within each series, the gas chromatographic behaviour of these components and their relationship to their molecular structures may be deduced.

Experimental

Determination of retention indices were carried out with a Perkin Elmer Chromatograph, model 900, equipped with a digital integrator SIP-1 and a counter, model 56. The detection system was flame ionization. Two stainless steel capillary columns were used. One polar, 150' x 0.01" coated with Carbowax 1540 + KOH (99:1), and the other non-polar 150' x 0.01" coated with squalane. Both were supplied by Perkin Elmer.

Most of the esters used were from Merck, Fluka and Schuchard. In some cases it was necessary to synthesise and purify them by normal laboratory methods.

The determinations were carried out in both columns at one temperature (81 °C). Full experimental conditions are given in an earlier publication [12].

Retention indices were calculated by the statistical process proposed by Grobler and Bálsiz [15]. For all the determinations, a series of five n-alkanes (nonane to tetradecane in Carbowax and hexane to decane in squalane) was used.

Retention indices of some one hundred esters are specific and, by conveniently grouping them, the gas chromatographic behaviour of the following homologous series may be studied: formates, acetates, propionates, butyrates, pentanoates, hexanoates, heptanoates, octanoates, nonanoates, isobutyrate, and isopentanoates; methyl, ethyl, propyl, butyl, pentyl, hexyl, isopropyl, isobutyl and isopentyl esters.

The graphs show the number of carbon atoms against retention index (I_R) of different homologous series, in every case, straight lines were obtained. These have very good correlation coefficients (approximately 0.9999), which prove the quality of the experimental determinations.

In addition it may be mentioned that the retention indices were determined many times over a period of three years. Values showed an average standard deviation of 0.02 %. No differences were found using two different capillary columns with the same stationary phase, nor when the chromatograph was changed.

Results

Retention Index of Straight Chain Esters

Table I groups the retention index of various esters which have been determined experimentally. Statistical calculations for the values are applied, considering as variables the carbon number of the acid (x), the carbon number of the alcohol (y) and retention index (I_R). The results appear in the following equations:

Carbowax

$$I_R = 87.30x + 88.64y + 557.10 \quad (1)$$

$$N = 63 \quad R = 0.993 \quad s = 27.59 \quad F = 2112.75$$

Squalane

$$I_R = 97.95x + 99.09y + 160.03 \quad (2)$$

$$N = 39 \quad R = 0.998 \quad s = 12.88 \quad F = 3769.48$$

where N = number of the esters employed; R = correlation coefficient, s = standard deviation and F = experimental value of Snedecor test.

Adding a fourth variable the boiling point of the ester, equations are obtained where the correlation and the standard deviation improve very slightly.

It can be deduced that I_R depends essentially on the length of the acid and the alcohol groups, the latter having a slightly greater influence.

Table II groups some of the equations for I_R vs the number of the carbon atoms in the ester. It can be observed that the values of the slopes of the series acetates, propionates and so forth are comparatively higher than the ethyl esters, propyl esters and the second series in each group. This is an additional indication that the length of the alcohol chains has a greater influence on I_R than the acid groups. This is also shown in Table III, where the I_R of various esters of complementary lengths of acid and alcohol are included.

Retention Index and Branching of Chain

The branching of the alcohol chain of an ester of n carbon number reduces the I_R in such a way that its value becomes closer to that of the ester with $n-1$ carbons than to that of the ester of n carbons. The branching of the acid chain also produces a lowering of I_R which acquires a value nearer to that of the ester with $n-1$ carbons, although this is less than for alcohol branching.

These variations may be observed in the corresponding values of Table I. The greater influence of the alkyl group of an alcohol, mentioned above, is again shown.

Using the same statistical processes previously summarised, the following equations for esters with branched chains can be derived for the variables I_R , x and y :

Carbowax

$$I_R = 93.63x + 98.70y + 392.13 \quad (3)$$

$$N = 15 \quad R = 0.997 \quad s = 10.68 \quad F = 1271.97$$

Squalane

$$I_R = 97.41x + 106.86y + 74.10 \quad (4)$$

$$N = 11 \quad R = 0.999 \quad s = 4.43 \quad F = 3491.15$$

In this case the contribution of the alkyl group is greater than that expressed in eqs. (1) and (2). Insufficient experimental data is at our disposal to be able to calculate the corresponding equations for the branched acid group.

I_R and the Relative Position of the Carboxylic Group

By grouping the esters with the same number of carbons and representing the values of their I_R versus the ratio number of carbon atoms in the acid (n_{ac})/number of carbon atoms in the alcohol (n_{al}). Thus $n_{ac}/n_{al} = z$, can be obtained — see Fig. 1. It is apparent that I_R reaches a minimum when the ratios are nearer to 1, that is, when the charge centre and the mass centre are as close as possible.

Statistical calculations in which the variables I_R , z , z^2 and the total number of carbon atoms in the ester (n) are included lead to the following equation.

Carbowax

$$I_R = -9.60z + 1.83z^2 + 87.30n + 560.47 \quad (5)$$

$$N = 50 \quad R = 0.996 \quad s = 19.62 \quad F = 1888.68$$

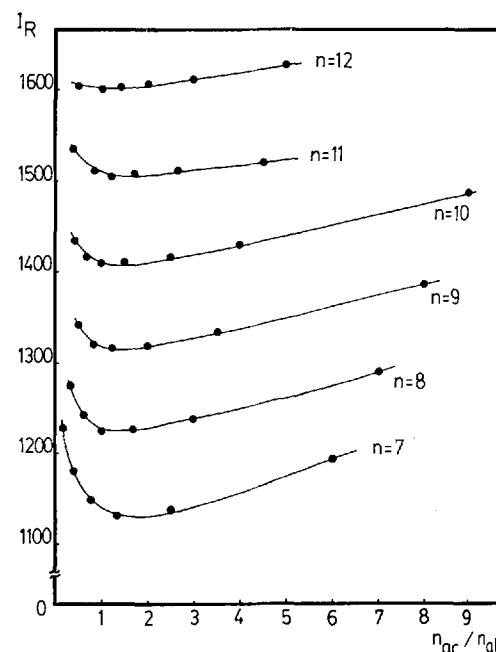


Fig. 1

I_R versus ratio of carbon number of acid to carbon number of alcohol (n_{ac}/n_{al}). Carbowax 1540 (Temp. = 81°C).

Table I. Retention index of esters (Temp. = 81 °C)

Compound	Carbowax 1540	Squalane
Methyl butyrate	994.5	661.3
Methyl pentanoate	1094.9	764.4
Methyl hexanoate	1192.5	864.8
Methyl heptanoate	1292.5	964.0
Methyl octanoate	1389.2	1064.0
Methyl nonanoate	1489.0	1163.8
Methyl decanoate	1587.5	1263.6
Ethyl butyrate	1043.1	739.2
Ethyl pentanoate	1141.1	840.2
Ethyl hexanoate	1236.3	938.9
Ethyl heptanoate	1337.2	1036.8
Ethyl octanoate	1432.5	1136.6
Ethyl nonanoate	1530.5	—
Ethyl decanoate	1628.0	—
Propyl butyrate	1129.8	837.5
Propyl pentanoate	1227.8	937.1
Propyl hexanoate	1320.0	1031.5
Propyl heptanoate	1420.7	1127.2
Propyl octanoate	1513.4	—
Propyl nonanoate	1612.3	—
Propyl decanoate	1708.7	—
Butyl butyrate	1223.4	936.3
Butyl pentanoate	1319.3	1034.6
Butyl hexanoate	1411.5	1127.0
Butyl heptanoate	1511.5	—
Butyl octanoate	1605.5	—
Butyl nonanoate	1701.2	—
Butyl decanoate	1796.8	—
Pentyl butyrate	1319.4	1034.4
Pentyl pentanoate	1415.5	1131.7
Pentyl hexanoate	1505.7	—
Pentyl heptanoate	1600.6	—
Pentyl octanoate	1693.8	—
Pentyl nonanoate	1786.9	—
Hexyl butyrate	1414.1	1132.9
Hexyl pentanoate	1511.5	—
Hexyl hexanoate	1599.6	—
Hexyl heptanoate	1693.9	—
Hexyl octanoate	1786.6	—
Propyl formate	931.3	560.8
Butyl formate	1028.5	665.9
Pentyl formate	1128.2	766.6
Hexyl formate	1227.2	868.9
Heptyl formate	1325.6	971.3
Octyl formate	1424.4	1073.6
Ethyl acetate	895.8	546.0
Propyl acetate	982.2	648.6
Butyl acetate	1080.3	751.7
Pentyl acetate	1179.7	852.1
Hexyl acetate	1275.9	950.3
Heptyl acetate	1374.7	1053.4
Octyl acetate	1472.7	1154.6
Ethyl propionate	963.1	645.7
Propyl propionate	1048.8	746.1
Butyl propionate	1146.1	846.8

Cont'd Table I

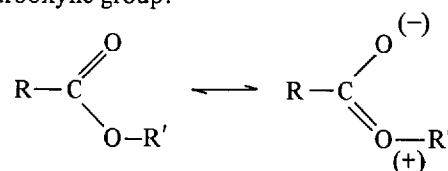
Pentyl propionate	1243.1	946.1
Hexyl propionate	1340.6	1044.4
Heptyl propionate	1437.9	1145.0
Octyl propionate	1535.1	—
Heptyl butyrate	1508.8	—
Octyl butyrate	1603.7	—
Heptyl pentanoate	1605.3	—
Octyl pentanoate	1700.0	—
Heptyl hexanoate	1692.4	—
Octyl hexanoate	1785.7	—
Isopropyl pentanoate	1140.2	878.7
Isopropyl hexanoate	1236.3	976.1
Isopropyl heptanoate	1337.2	1074.8
Isopropyl octanoate	1433.2	1173.2
Isopropyl nonanoate	1529.9	—
Isopropyl decanoate	1626.9	—
Isobutyl butyrate	1165.1	898.6
Isobutyl pentanoate	1260.5	994.9
Isobutyl hexanoate	1352.7	1090.9
Isobutyl heptanoate	1452.4	1186.9
Isobutyl octanoate	1546.3	1283.0
Isobutyl nonanoate	1641.7	—
Isopentyl butyrate	1269.3	999.9
Isopentyl pentanoate	1357.5	1093.1
Isopentyl hexanoate	1435.9	1184.8
Isopentyl heptanoate	1516.8	—

Table II. Retention index (I_R) vs carbon number atoms of ester (n) for homologous series (temp. = 81 °C)

Serie	Carbowax 1540	Squalane
Acetates	I _R = 98.07 n + 492.07	I _R = 100.55 n + 147.10
Ethyl esters	I _R = 97.49 n + 458.10	I _R = 99.15 n + 145.15
Propionates	I _R = 97.26 n + 465.29	I _R = 99.74 n + 147.64
Propyl esters	I _R = 96.49 n + 454.39	I _R = 95.69 n + 170.34
Butyrates	I _R = 95.35 n + 460.81	I _R = 98.44 n + 148.55
Butyl esters	I _R = 94.05 n + 471.61	I _R = 93.90 n + 188.03
Pentanoates	I _R = 94.73 n + 468.59	I _R = 97.20 n + 159.70
Pentyl esters	I _R = 93.15 n + 482.83	I _R = 89.74 n + 226.75
Hexanoates	I _R = 93.30 n + 479.55	—
Hexyl esters	I _R = 92.75 n + 488.15	—

Discussion

The results can best be understood by taking into account the structure of esters where the polarity is centred on the carboxylic group:



The polarity will depend on the nature of R and R', which, as alkyl groups, will have an +I inductive effect, tending to diminish the polarity, bearing in mind that the inductive effect increases with the length and branching of the alkyl group.

The +I effect of the radicals R and R' are additive. It can be assumed that the carboxylic group on its own has a polarity, P, and if r and r' are the negative contributions of the radicals, the total polarity of the ester (p) would be:

$$(p) = P - (r + r')$$

Table III. Retention index of esters of complementary lengths of acid and alcohol (Temp. = 81 °C)

Compound	Carbowax 1540	Squalane
Heptyl acetate	1374.7	1053.4
Ethyl heptanoate	1337.2	1036.8
Pentyl propionate	1243.4	946.1
Propyl pentanoate	1227.8	937.1
Hexyl formate	1227.2	868.9
Methyl hexanoate	1192.5	864.8
Butyl acetate	1080.3	751.7
Ethyl butyrate	1043.1	739.2
Butyl formate	1028.5	665.9
Methyl butyrate	994.5	661.3

The values of I_R will increase as the length of the chain and the polarity of ester increase. The experimental data show that I_R depends on the length and the structure of R and R'.

As can be seen from the results above, for an ester with a given number of carbon atoms, R' is slightly more important than R. This shows that the inductive +I effect of R' will be greater than R, which could have been assumed from its position in relation to the charge centres of the carboxylic group. In order to give numerical values to these corresponding inductive effects for the alcoholic (R') and acidic (R) chains, arbitrary values can be assigned. In the Carbowax eqs. (1) and (3), the values would be:

$$\begin{aligned} \text{Carbon atom of R in a linear chain} &= \\ &= 1.016 (88.64/87.30) \end{aligned}$$

$$\begin{aligned} \text{Carbon atom of R in a branching chain} &= \\ &= 1.054 (98.70/93.63) \end{aligned}$$

$$\text{Carbon atom of R' in both chains} = 1.000$$

This can be applied to specific cases as shown in Table IV.

Thus it can be seen that there exists a direct relation between the differences in polarity of two esters and differences in their I_R. The differences between the values of I_R in squalane will be less due to the non-polarity of this column, as shown in Table IV.

As has already been shown, branching of the chain causes reduced retention. Logically, an isopropyl ester will have a lower I_R than a propyl ester since the isopropyl radical has a higher +I effect which means a lower polarity.

Table IV. Relation between polarity and I_R of esters

Compound	r	r'	Estimated polarity		Carbowax 1540		Squalane	
			(p)	Δ(p)	I _R	ΔI _R	I _R	ΔI _R
Pentyl propionate	3.048	5	16.952	0.032	1243.4	15.6	946.1	9.0
Propyl pentanoate	5.080	3	16.920		1227.8		937.1	
Hexyl acetate	2.032	6	16.968	0.068	1275.9	39.6	950.3	11.4
Ethyl hexanoate	6.096	2	16.904		1236.3		938.9	
Butyl formate	1.016	4	19.984	0.048	1028.5	34.5	665.9	4.6
Methyl butyrate	4.064	1	19.936		994.5		661.3	
Isopropyl butyrate	4.216	3	17.784	- 0.152	1044.9	84.9	779.3	58.2
Propyl butyrate	4.064	3	17.936		1129.8		837.5	
Isobutyl butyrate	4.216	4	16.784	- 0.152	1165.1	58.3	898.8	37.5
Butyl butyrate	4.064	4	16.936		1223.4		936.3	
Isopentyl butyrate	4.216	5	15.784	- 0.152	1269.3	50.1	999.9	34.5
Pentyl butyrate	4.064	5	15.936		1319.4		1034.4	

Aleatory value of polarity of carboxylic group (P) = 25

Table V. Retention index of isoesters (Carbowax 1540, Temp. = 81°C)

Compound	I _R
Isopropyl pentanoate	1140.2
Propyl isopentanoate	1158.3
Propyl pentanoate	1227.8
Isopropyl butyrate	1044.9
Propyl isobutyrate	1088.4
Propyl butyrate	1129.8
Isopropyl isopentanoate	1075.9

In Table V are collected the variations produced in the I_R by branching of the alkyl acid group. It can be observed that the reduction in this case is less than that produced by a branching of the alkyl group of the alcohol. In the case of isopropyl isopentanoate, where both effects are seen together, a minimum value for I_R is produced.

In the calculation shown above for an ester with n carbon atoms, the conclusion would be that the ester with the longer alcohol chain would have a higher I_R. The value of I_R should increase in a linear fashion according to the length of the alcohol chain. However, the experimental results in Fig. 1 show that this is not true.

This phenomenon could be explained by the steric effects of R and R'. When the carboxylic group is in the central position, the alkyl chains of R and R' cover the charge centre which makes interaction with the charge centres of the stationary phase more difficult, thereby diminishing the attractive forces and, therefore, the I_R.

This discussion refers mainly to Carbowax, but can be extended to squalane as well, although here the effects can be expected to be less due to non-polarity.

Conclusion

It can be concluded that the values of the retention indices are affected firstly by the number of acid and alcohol carbons. Secondly, the +I inductive effect of the alkyl radicals of acid and alcohol have an effect and thirdly the position of the alkyl group will also affect I_R owing to steric effects. All these effects are greater when the polarity of the stationary phase is higher.

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Received: July 31, 1980

Accepted: Oct. 14, 1980

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