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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

PART II. UNSATURATED ESTERS

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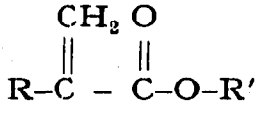
SUMMARY

The retention behaviour of several series of unsaturated homologous esters on a non-polar stationary phase is reported together with correlations that are possibly due to the structure of the compounds, and the influence of the boiling point is considered.

INTRODUCTION

The retention behaviour of simple aliphatic esters of which both alkyl groups vary in chain length and have either straight or branched chains has been reported[1].

While retention data of many individual unsaturated esters have been reported, the most extensive work concerns the α-alkylacrylic esters[2] which, following our earlier nomenclature, are represented as:



where R and R′ are alkyl groups characteristic of the reactant acid and alcohol, respectively.

Gas chromatography of the methyl esters of several C_4 to C_6 unsaturated esters has been reported by JANAK *et al.*[3]. The data determined on a Silicone E-301 stationary phase have been shown as a plot of relative retention volume *versus* boiling point of the esters.

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In this work the behaviour of several types of homologous series of unsaturated esters is described.

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 trans-esterification procedures with an acidic ion-exchange resin as catalyst and were fractionated before use.

Gas chromatography

The retention data were obtained isothermally at 150° using a 12 ft. × ¼ in. O.D. aluminium column packed with 10% Methyl Silicone Polymer SE-30 on 60–80 mesh acid-washed and silanised Celite 560. The equipment, conditions and calibration procedures were as previously reported[1].

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

DISCUSSION OF RESULTS

The influence of a double bond in the acid chain (R) may be established by

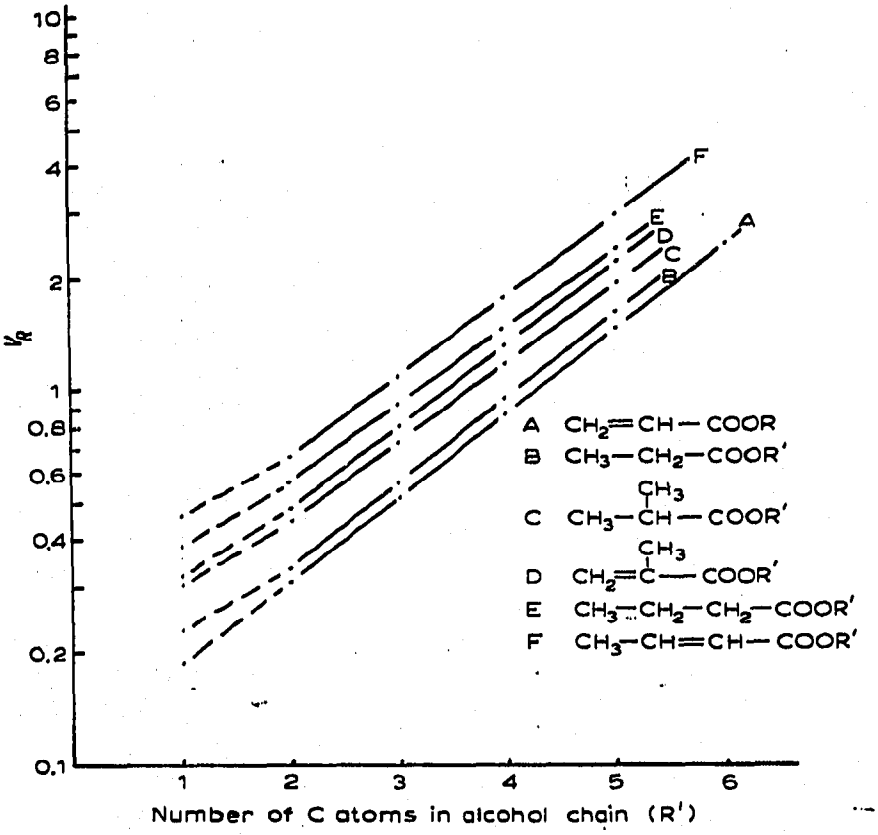

Fig. 1. Plots of logarithm of relative retention of unsaturated esters with varying alcohol chain (R') length and with the acid chain (R) both branched and linear.

TABLE I

RETENTION DATA FOR UNSATURATED ESTERS

Ester	V_g[a]	V_R[b]	I_R
Ethyl crotonate	0.441	0.667	820
Propyl crotonate	0.710	1.075	917
Isopropyl crotonate	0.540	0.818	863
Butyl crotonate	1.190	1.804	1021
2-Methylpropyl crotonate	0.978	1.481	983
Amyl crotonate	1.905	2.89	1119
3-Methylbutyl crotonate	1.610	2.44	1082
Methyl acrylate	0.128	0.194	569
Ethyl acrylate	0.205	0.310	664
Butyl acrylate	0.595	0.903	878
Amyl acrylate	0.960	1.455	978
Hexyl acrylate	1.595	2.42	1068
Methyl methacrylate	0.217	0.329	677
Ethyl methacrylate	0.320	0.482	756
Propyl methacrylate	0.528	0.798	856
Butyl methacrylate	0.884	1.34	962
Amyl methacrylate	1.460	2.212	1064
Hexyl methacrylate	2.400	3.64	1165
2-Methylpropyl methacrylate	0.750	1.135	928
Vinyl acetate	0.115	0.173	548
Vinyl propionate	0.190	0.286	648
Vinyl butyrate	0.310	0.466	750
Isopropenyl acetate	0.185	0.274	644

[a] Corrected for dead volume.
[b] Relative to nonane.

comparison of the homologous acrylate, methacrylate and crotonate esters with the propionate, isobutyrate and butyrate esters as shown in Fig. 1. It is apparent that a series of linear plots were obtained. The slopes of the saturated esters were essentially parallel (*i.e.* the slope of the propionate ester line was slightly greater than that of the butyrate esters) while the slope representing the propionate esters was almost parallel to that of the acrylate esters and the slope of the crotonate ester plot was greater than for the butyrate ester plot.

From Table I a comparison of retention indices of the various esters shows that when the number of carbon atoms in the acid chain (R) is two, the retention index is reduced by 10–15 units by the presence of a double bond, but when R is three, the retention is increased by 30–40 units.

The retention indices of the unsaturated esters were found to increase by 100 units per methylene group as compared to 95 units for the butyrate esters. The near parallel plots of the acrylate and propionate esters occur as the propionate esters increase by approximately 100 units per methylene group.

When the hydrogen on the α-carbon atom of the acrylate esters was replaced by a methyl group (the methacrylate esters), the retention index was increased by 100 units. However, when the hydrogen on the β-carbon atom was replaced by a methyl group (the crotonate esters) the retention index increased by 130–140 units.

The effect of a double bond in the alcohol chain (R′) was observed by considering the retention of vinyl acetate, propionate and butyrate with that of ethyl acetate,

TABLE II

EFFECT OF THE PRESENCE OF A DOUBLE BOND IN THE ALCOHOL CHAIN OF UNSATURATED ESTERS

Ester	V_g	V_R	I_R	ΔI_R
Vinyl acetate	0.115	0.173	548	23
Ethyl acetate	0.130	0.200	571	
Vinyl propionate	0.190	0.286	648	31
Ethyl propionate	0.220	0.335	679	
Vinyl butyrate	0.310	0.466	750	38
Ethyl butyrate	0.375	0.565	788	
Isopropenyl acetate	0.185	0.274	644	19
Isopropyl acetate	0.170	0.259	625	

propionate and butyrate. The results are shown in Table II. As the number of carbon atoms in the acid chain increases the amount by which the double bond reduces the retention of the *n*-alkyl esters increases from 20 to 40 units. The data are plotted in Fig. 2 and the larger slope of the ethyl ester plot is apparent, the increase in retention per methylene group being approximately 108 and 100 units for the ethyl and vinyl esters, respectively.

The effect of a double bond in the acid chain and a branched alcohol chain was examined by considering retention data of the *n*-alkyl and isoalkyl crotonates as shown in Fig. 3.

The deviation from linearity observed previously with saturated isopropyl esters is observed while the reduction in retention was slightly less than observed for the *n*-alkyl esters. The reductions in the retention indices of the unsaturated and saturated esters were 54, 38 and 37 units and 60, 40 and 40 units for the isopropyl, isobutyl and isopentyl esters respectively.

While it has been shown[1] that the retention behaviour of the saturated esters on a non-polar stationary phase are closely related to the boiling points of the

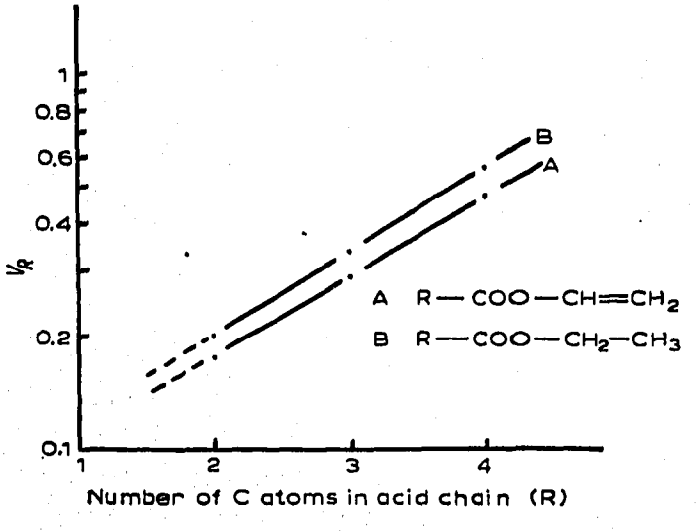

Fig. 2. Plots of logarithm of relative retention of vinyl esters and corresponding saturated esters.

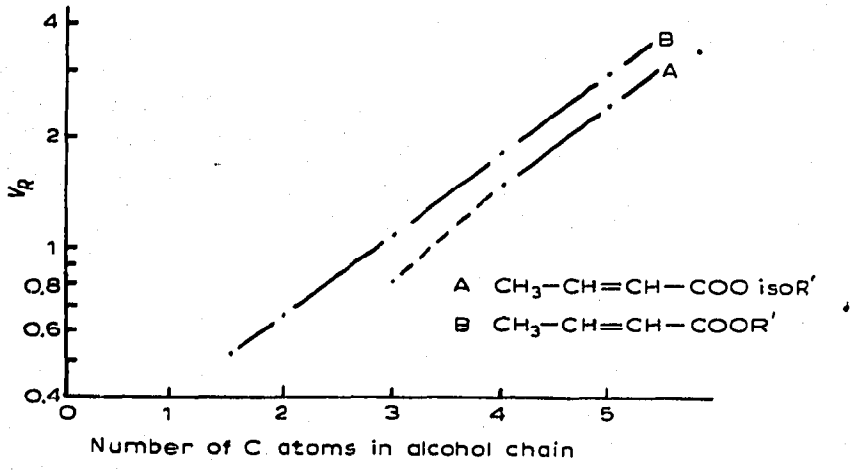

Fig. 3. Plots of logarithm of relative retention of *n*-alkyl and isoalkyl crotonates.

compounds, it is now apparent that with unsaturation two further effects are experienced. The presence of a double bond in an alkyl group tends to decrease the retention as has been shown with fatty esters, the decrease being accentuated where conjugation occurs.

The *n*-alkylacrylic esters have lower retention indices than the corresponding *n*-alkyl propionates and as the boiling points of the two series are almost identical the decreased retention may be attributed to unsaturation and the presence of conjugation between the double bond and the neighbouring carboxyl group.

The retention indices of the crotonate esters are substantially higher than those of the corresponding butyrates. While the retention is reduced by the conjugated unsaturation, the 20° temperature difference between the boiling points of the crotonate and butyrate esters is the predominant effect. Similarly the methacrylate esters have slightly higher boiling points than the isobutyrate esters and increased retention occurs.

With unsaturated isoalkyl esters reduction in retention of the isopropyl ester was observed, but the reduction in retention with respect to the parent *n*-alkyl esters was lower with the unsaturated than with the saturated esters. The effect may be explained by the relative variations of the boiling points of the esters as well as by the branching of both alkyl chains, *e.g.* isobutyl methacrylate has a larger retention index than isobutyl isobutyrate but also a 6° difference in boiling point.

The presence of unsaturation in the alcohol chain causes a decrease in retention. Vinyl acetate (typical of the vinyl esters) is of lower boiling point than ethyl acetate (*i.e.* 4°) and the reduced retention can be attributed to the effect of boiling point and to the double bond. As the double bond is separated from the carboxyl group no added influence of conjugation is experienced. With the double bond adjacent to a methyl group in the alcohol chain (*i.e.* isopropenyl acetate) an increase in retention of approximately 20 units compared to the saturated branched-chain ester (isopropyl acetate) is observed and here a higher boiling point is exhibited by the unsaturated ester.

REFERENCES

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2 J. K. HAKEN, T. R. MCKAY AND P. SOUTER, *J. Gas Chromatog.*, 3 (1965) 61.
3 J. JANAK, M. DOBIASOVA AND K. VERES, *Collection Czech. Chem. Commun.*, 25 (1960) 1566.