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THE RETENTION BEHAVIOUR OF ISOMERIC BUTENOIC ACID ESTERS ON STATIONARY PHASES OF VARYING POLAR CHARACTER

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SUMMARY

The retention behaviour of the isomeric short-chain unsaturated butenoic acid esters is reported on polysiloxane stationary phases which vary in character from essentially non-polar to those of considerable polar character.

INTRODUCTION

The gas chromatography (GC) of unsaturated fatty esters has been extensively studied and relationships generally dependent on the additivity of non-interacting structural units have been reported and included in recent reviews[1-3]. These relationships are of considerable value as aids in tentative identification as the unsaturation of the naturally occurring fatty esters tends to be concentrated near the centre of the alkyl chains. However, with the availability of retention data of complete series of isomeric fatty esters it is evident that where unsaturation occurs near the chain extremities significant interactions occur and the simple relationships are not applicable[3,4]. It is now evident that three sections of the chain must be considered, a central region where simple additivity is applicable, near the carbonyl group and at the chain end near the terminal methyl group[5]. For the relatively short-chain butenoic acid esters the proximity of unsaturation and the chain ends may be expected to have a marked effect on the retention behaviour.

While retention data of many individual butenoic acid esters have been reported[6] systematic studies of lower isomeric unsaturated esters series have not been extensively reported. The GC of the methyl esters of several C_4 to C_5 unsaturated compounds has been reported by JANÁK and his co-workers[7] on a polar (Reoplex 400) and two non-polar phases (dimethyl polysiloxane and squalane) at several temperatures together with a plot of relative retention and boiling point of the esters.

Retention data of *n*-alkyl methacrylate esters from C_2 to C_{18} and *n*-alkyl, α-alkyl acrylic esters have been reported by GUILLET and co-workers[8] and by HAKEN AND MCKAY[9], respectively, both using non-polar stationary phases.

The methyl esters of some isomeric *n*-hexenoic acids have been examined by FELL and co-workers[10] who reported difficulty in separating the *cis*-3- and *cis*-4-isomers using a capillary column containing a polar stationary phase.

Certain unsaturated butenoic acid esters have been studied on non-polar[11]

TABLE I

RETENTION DATA FOR ISOMERIC BUTENOIC AND BUTYRIC ACID ESTERS

Compound	*Gensil S2116*			*OV-1*		
	V_g	V'_R	I_R	V_g	V'_R	I_R
Methyl-2-methyl-2-propenoate	0.250	0.292	650	0.217	0.320	677
Ethyl-2-methyl-2-propenoate	0.311	0.444	742	0.320	0.482	756
Propyl-2-methyl-2-propenoate	0.535	0.704	851	0.528	0.708	856
Butyl-2-methyl-2-propenoate	0.933	1.333	947	0.884	1.34	962
Pentyl-2-methyl-2-propenoate	1.553	2.220	1068	1.46	2.212	1064
Hexyl-2-methyl-2-propenoate	2.703	3.861	1174	2.46	3.64	1165
Octyl-2-methyl-2-propenoate	7.815	11.155	1380			
Isopropyl-2-methyl-2-propenoate	0.368	0.528	776			
Isobutyl-2-methyl-2-propenoate	0.743	1.062	912	0.750	1.135	928
Isopentyl-2-methyl-2-propenoate	1.317	1.882	1031			
Methyl-2-butenoate	0.205	0.422	732			
Ethyl-2-butenoate	0.443	0.633	811	0.441	0.667	820
Propyl-2-butenoate	0.771	1.102	929	0.716	1.075	917
Butyl-2-butenoate	1.320	1.886	1033	1.166	1.864	1021
Pentyl-2-butenoate	2.206	3.272	1142	1.965	2.86	1116
Hexyl-2-butenoate	3.829	5.470	1245			
Octyl-2-butenoate	11.116	15.886	1458			
Isopropyl-2-butenoate	0.557	0.766	858	0.546	0.818	863
Isobutyl-2-butenoate	1.048	1.407	985	0.978	1.481	983
Isopentyl-2-butenoate	1.845	2.635	1100	1.61	2.44	1082
Methyl-3-butenoate	0.204	0.291	658	0.253	0.362	693
Ethyl-3-butenoate	0.314	0.446	742	0.359	0.514	767
Propyl-3-butenoate	0.526	0.756	848	0.567	0.816	864
Butyl-3-butenoate	0.937	1.338	964	0.953	1.362	967
Pentyl-3-butenoate	1.507	2.281	1066	1.544	2.205	1065
Hexyl-3-butenoate	2.692	3.845	1174	2.450	3.566	1166
Octyl-3-butenoate	7.741	11.070	1396	6.328	9.646	1357
Isopropyl-3-butenoate	0.364	0.520	773	0.431	0.616	866
Isobutyl-3-butenoate	0.743	1.062	914	0.788	1.125	926
Isopentyl-3-butenoate	1.284	1.844	1028	1.454	2.077	1050
Methyl butyrate	0.222	0.317	671	0.266	0.307	714
Ethyl butyrate	0.342	0.486	761	0.375	0.565	788
Propyl butyrate	0.616	0.871	873	0.665	0.926	884
Butyl butyrate	1.038	1.483	983	0.975	1.486	986
Pentyl butyrate	1.772	2.532	1091	1.550	2.350	1075
Hexyl butyrate	3.031	4.330	1202			
Octyl butyrate	8.747	12.405	1415			
Isopropyl butyrate	0.413	0.590	796	0.450	0.686	823
Isobutyl butyrate	0.821	1.173	934	0.786	1.186	937
Isopentyl butyrate	1.436	2.052	1047	1.366	1.976	1039
Methyl isobutyrate	0.178	0.254	627	0.216	0.319	669
Ethyl isobutyrate	0.261	0.373	705	0.295	0.445	738
Propyl isobutyrate	0.456	0.651	817	0.475	0.722	836
Butyl isobutyrate	0.783	1.119	928	0.770	1.170	933
Pentyl isobutyrate	1.328	1.807	1033	1.265	1.870	1032
Hexyl isobutyrate	2.251	3.216	1142			
Octyl isobutyrate	6.388	9.125	1353			
Isopropyl isobutyrate	0.306	0.429	730	0.370	0.565	785
Isobutyl isobutyrate	0.634	0.905	885	0.660	0.967	900
Isopentyl isobutyrate	1.105	1.579	998	1.056	1.590	998

OV-17			*85% Phenyl*			*OV-210*			*XF-1150*		
V_g	V_R	I_R	V_g	V_R	I_R	V_g	V_R	I_R	V_g	V_R	I_R
0.210	0.680	820	0.248	0.820	869	0.300	1.000	900	0.542	1.806	1046
0.240	0.830	863	0.352	1.173	935	0.400	1.333	969	0.681	2.270	1102
0.402	1.34	957	0.545	1.818	1020	0.628	2.093	1075	1.004	3.345	1200
0.690	2.30	1068	0.914	3.045	1140	0.944	3.145	1175	1.464	4.880	1207
1.23	3.97	1176	1.487	4.955	1217	1.458	4.860	1280	2.255	7.515	1401
2.07	6.68	1281	2.589	8.630	1310	2.202	7.340	1370	3.420	11.400	1500
5.10	17.00	1463	7.320	24.420	1520	5.043	16.810	1578	7.524	25.080	1702
			0.352	1.173	935	0.450	1.500	995	0.723	2.410	1114
0.620	1.94	1032	0.723	2.410	1074	0.833	2.775	1145	1.248	4.160	1251
4.05	13.51	1416	1.131	3.770	1160	1.272	4.240	1247	1.872	6.240	1354
			0.390	1.301	959	0.475	1.584	1000	0.900	3.000	1170
0.430	1.30	965	0.550	1.833	1021	0.638	2.125	1080	1.140	3.700	1230
0.670	2.23	1065	0.853	2.842	1100	1.004	3.345	1190	1.692	5.640	1320
1.10	3.67	1157	1.487	4.955	1217	1.488	4.960	1280	2.580	8.600	1433
1.84	6.13	1265	2.476	8.253	1306	2.265	7.550	1384	3.984	13.280	1545
			3.960	13.200	1407	3.342	11.140	1479	5.807	19.355	1641
			9.825	32.750	1580	7.401	24.670	1672	12.780	42.600	1838
0.435	1.50	978	0.550	1.834	1022	0.698	2.327	1104	1.158	3.861	1232
0.900	2.80	1094	1.013	3.375	1138	1.290	4.300	1251	2.037	6.790	1373
1.413	4.71	1208	1.811	6.035	1251	0.188	6.025	1353	3.300	11.000	1406
0.182	0.607	801	0.255	0.850	872	0.335	1.115	927	0.675	2.250	1100
0.261	0.869	871	0.358	1.194	940	0.468	1.560	1006	0.849	2.830	1150
0.433	1.442	971	0.606	2.020	1040	0.700	2.303	1106	1.275	4.250	1250
0.723	2.410	1072	1.029	3.430	1141	1.096	3.652	1211	1.836	6.120	1301
1.205	4.015	1173	1.698	5.650	1239	1.667	5.555	1310	2.714	9.045	1448
1.965	6.550	1271	2.777	9.255	1332	2.498	8.328	1420	4.023	13.410	1548
5.256	17.520	1460	7.290	24.300	1520	5.595	18.650	1614	8.685	28.950	1740
0.300	1.000	900	0.402	1.340	963	0.511	1.703	1025	0.862	2.872	1160
0.567	1.890	1023	0.737	2.455	1075	0.900	3.000	1160	1.500	5.000	1300
0.987	3.289	1133	1.364	4.545	1190	1.356	4.521	1256	2.241	7.470	1400
0.190	0.630	811	0.219	0.730	845	0.326	1.086	902	0.541	1.803	1043
0.290	0.93	887	0.333	1.109	926	0.445	1.482	992	0.697	2.322	1108
0.440	1.57	987	0.543	1.811	1020	0.677	2.258	1096	1.093	3.644	1215
0.690	2.47	1081	0.930	3.100	1122	1.010	3.305	1193	1.607	5.355	1313
1.150	4.11	1182	1.463	4.875	1205	1.520	5.065	1290	2.437	8.024	1418
2.070	6.704	1281	2.280	7.600	1297	2.310	7.700	1388	3.638	12.125	1520
5.05	18.10	1475	6.303	21.010	1492	4.995	16.650	1576	8.058	26.860	1716
0.320	1.07	915	0.375	1.250	953	0.527	1.757	1036	0.696	2.321	1108
0.500	1.67	1036	0.660	2.200	1257	0.910	3.034	1168	1.316	4.387	1262
0.995	3.32	1140	1.221	4.070	1172	1.367	4.555	1261	2.013	6.710	1350
–	–	–	0.168	0.561	796	0.270	0.910	882	0.393	1.311	963
0.213	0.71	838	0.256	0.853	878	0.373	1.244	951	0.520	1.734	1032
0.340	1.13	926	0.388	1.292	959	0.584	1.947	1060	0.775	2.583	1131
0.550	1.83	1024	0.651	2.170	1058	0.856	2.854	1152	1.179	3.931	1235
0.930	3.10	1125	1.042	3.472	1147	1.298	4.327	1248	1.788	5.960	1340
1.482	4.94	1220	1.751	5.835	1246	1.380	6.400	1345	2.733	9.110	1443
4.110	13.28	1416	4.536	15.120	1430	4.374	14.580	1543	6.030	20.100	1642
0.240	0.77	850	0.256	0.853	878	0.400	1.303	973	0.517	1.723	1031
0.460	1.49	980	0.483	1.609	1000	0.702	2.339	1104	0.993	3.310	1102
0.760	2.46	1080	0.813	2.709	1100	1.151	3.838	1221	1.510	5.032	1200

and polar[12] stationary phases. On non-polar phases the behaviour of the esters was analogous to their boiling points and a decrease in retention with respect to the saturated ester was apparent. The effect of increasing the polarity of the stationary phase was to increase the retention of the unsaturated ester with respect to the saturated one.

The present work reports the retention behaviour of the *n*-alkyl esters of the three series of isomeric butenoic acids, *i.e.* *trans*-2-butenoate esters (crotonate esters), 3-butenoate esters (vinyl acetic acid esters) and 2-methyl-2-propenoate esters (methacrylate esters) on polysiloxane stationary phases of increasing polar character.

EXPERIMENTAL

Preparation of esters

The esters where available were of commercial quality and of substantial purity. The remainder of the esters were prepared using esterification or transesterification procedures with an acidic ion-exchange resin as catalyst.

Chromatography

The retention data were obtained isothermally at 150° using 12 ft. × 1/4 in. O.D. aluminium columns packed with 10% stationary phase on 60–80 mesh acid washed and silanised Celite 500. The equipment, conditions and calibration procedures were as previously reported[11].

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

The stationary phases used in order of increasing general polar character were: (a) Gensil S2110, methyl (70%) stearoyl (30%) polysiloxane; (b) OV-1, dimethyl polysiloxane; (c) OV-17, methyl (50%) phenyl (50%) polysiloxane; (d) 85% phenyl polysiloxane, methyl (15%) phenyl (85%) polysiloxane; (e) OV-210, methyl (50%) trifluoropropyl (50%) polysiloxane; (f) XF-1150, methyl (50%) cyanoethyl (50%) polysiloxane.

The Gensil S2110 was provided by General Silicones Pty. Ltd. Chatswood N.S.W. and the 85% phenyl-substituted polysiloxane was an experimental product provided by the Ohio Valley Specialty Chemical Co. The physical characteristics and Rohrschneider Constants of these materials have been described previously[13].

DISCUSSION OF RESULTS

The retention behaviour of the isomeric butenoic acid esters is shown in Fig. 1 where plots of the logarithm of the relative retention of the esters *versus* the number of carbon atoms in the alcohol chain (R′) are shown determined on stationary phases of varying polar character. The alcohol chain length (R′) is the carbon number of the esterifying alcohol as previously described[11], similarly the acid chain length (R) is the carbon number of the parent acid less the carbon atom associated with the carbonyl group with the butenoic acids R is equal to three.

On the non-polar phases OV-1 and Gensil S2110 (Figs. 1a and 1b) considerable variation in retention of the three series of isomers is apparent. The 2-butenoic acid

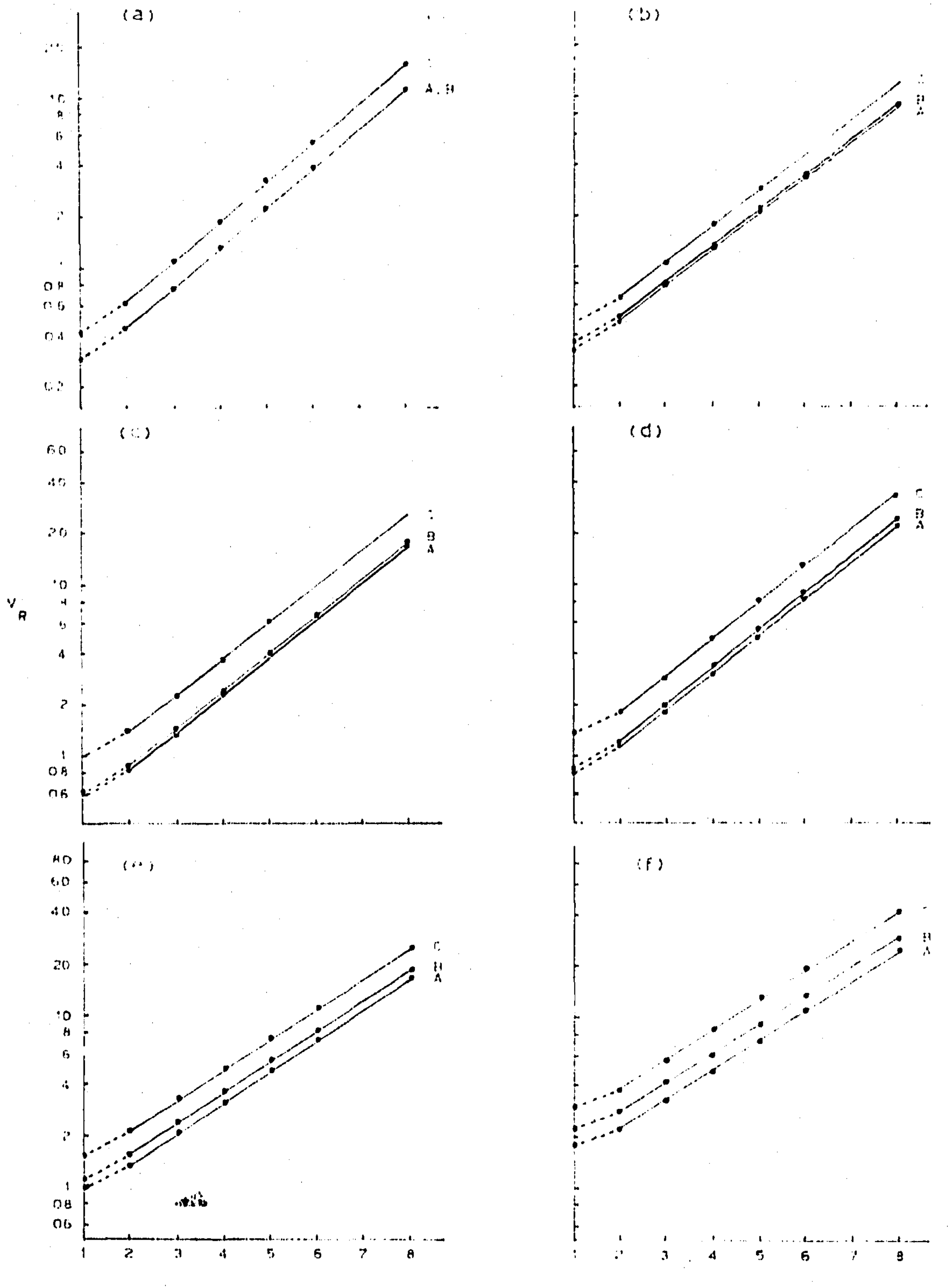

Fig. 1. Retention plots of (A) 2-methyl-2-propenoic, (B) 3-butenoic, and (C) *trans*-2-butenoic acid esters with (a) Gensil S2116, (b) OV-1, (c) OV-17, (d) 85% phenyl, (e) OV-210 and (f) NF-1150 stationary phases.

esters exhibit a marked increase in retention when compared to the other esters. This was expected from a study of the respective boiling points[11], as the 2-butenoic acid esters were at least 20° higher in boiling point than the other isomers. This large difference could not be attributed to the presence of conjugation which would result in a higher polarisability of the system, as the 2-methyl-2-propenoic acid esters and the *cis*-isomer of the 2-butenoic acid esters had boiling points similar to the 3-butenoic acid esters. It was apparent that the boiling points were effected by the shape of the molecules and the resultant steric hindrance. The 3-butenoic, 2-methyl-2-propenoic and the *cis*-2-butenoic acid esters (retention data of the latter ester series were not available, however the boiling points of the acid and ethyl ester were[14]) were all capable of forming compact molecules due to rotation around the single bond in the acid chain. This would result in a reduction in the surface area of the molecule and its cohesive forces[15]. Similarly screening of the carbonyl oxygen by the acid chains in the ester series[16] was possible which again would result in a lowering of the boiling points of these esters. The *trans*-2-butenoic acid esters were the only series of esters where rotation of the acid chain did not affect the shape of the molecule or sterically hinder the carbonyl oxygen group and hence is a likely reason why their boiling points are higher than the other isomers.

The effect of stationary phase polarity on the ester series is shown in Fig. 1 where the polarity of the phases increases from the non-polar Gensil S2116 to the highly polar XF-1150 stationary phase.

The polar substituent in the stationary phases varied in nature from the electron-donor phenyl group to the electron-acceptor cyanoethyl or trifluoropropyl groups. The effect of these donor and acceptor groups in the phases on the retention of saturated esters has been previously discussed[13]. It is evident that the effect of the substituents on the retention of the butenoic acid esters will be analogous to that of the saturated esters as retention plots of the unsaturated ester series examined here on acceptor phases (Figs. 1e and f) have lower slopes than the plots on non-polar (Figs. 1a and b) and donor phases (Figs. 1c and d).

It is apparent that as the general polarity of the phase increases the retention of the *trans*-2-butenoic and the 3-butenoic acid ester series increases with respect to the 2-methyl-2-propenoic acid ester series, even though the latter series is conjugated and should be a more polarisable system than the 3-butenoic acid ester series. It again appears that steric hindrance accounts for this unexpected behaviour. The acid chain of the *trans*-2-butenoic acid esters cannot screen the carbonyl oxygen and would be expected to be susceptible to change in polarity as it is a highly polarisable system. The 3-butenoic and 2-methyl-2-butenoic acid esters are capable of screening the carbonyl oxygen, however the 3-butenoic acid esters possess fewer orientations where screening is possible and apparently are still affected by changes in column polarity. The 2-methyl-2-propenoates are likely to be sterically hindered to a greater extent than the other ester series studied here, due to their basic structure. The resultant screening of the carbonyl oxygen is sufficient to prevent this polarisable ester series to be as susceptible to changes in column polarity as the other butenoic acid ester series.

When the retention behaviour of the butenoic acid esters is compared with that of the corresponding saturated esters *i.e.* butyrates and isobutyrates, on columns of varying polarity the retention behaviour is similar to that of the long chain fatty esters in so much as the retention is increased as the polar character of the column is increased.

The 3-butenoic acid esters follow the usual pattern of the fatty esters where on low and medium polarity columns, such as OV-17, the retention is lower than that of the corresponding butyrate esters, while with phases of increased polar character the retention is greater with the unsaturated esters.

The retention of the 2-butenoate esters is greater than that of the corresponding butanoates on all phases, the increases tending to be greater with increased polar nature of the phase. The increased retention of these compounds as compared with the 3-butenoates is as widely reported with isomeric fatty esters[3].

Retention of the esters of the branched chain unsaturated isomer follows the pattern of the 2-butenoate ester, *i.e.* increases in retention being greater with the more polar phases.

WALRAVEN[17] and WALRAVEN *et al.*[18,19] have shown that isomers of homologous compounds form staggered parallel imbrication plots or roofing tile patterns for each carbon number when examined on two stationary phases. It has subsequently been shown that linearity occurs only when retention is an additive effect where interactions are not significant[20] and as would be expected plots of the isomeric butenoate esters do not produce plots that approach linearity.

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