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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

IX*. STRUCTURE-RETENTION INCREMENTS OF UNSATURATED ESTERS

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SUMMARY

The influence of the polarity of the stationary phase on retention increments of homologous and isomeric unsaturated esters is detailed and the results are discussed in terms of the findings of earlier studies that have been reported where restricted ranges of solutes and solvents were considered.

INTRODUCTION

The gas chromatography of unsaturated long-chain esters has been extensively studied and relationships generally dependent on the additivity of structural units have been reported. The relationships which have been the subject of several reviews¹⁻³ have largely concerned the naturally occurring fatty esters where the unsaturation is usually methylene-interrupted and tends to be concentrated near the centres of the alkyl chains. The availability of more extensive retention data of isomeric esters has shown that the earlier relationships are not generally applicable and where unsaturation is near the chain extremities significant interactions occur^{3,4}. It has been demonstrated qualitatively that three sections of the chain should be considered, a central region where the additive relationships are applicable, near the carbonyl group and near the chain end⁵. Reports periodically appear⁶ showing the retention behaviour of complete homologous series of fatty esters and a more detailed study than currently presented showing the influence of unsaturation along a chain may soon be possible.

With the shorter-chain esters the proximity of the chain extremities and the unsaturation might be expected to have a marked effect on the retention behaviour.

The gas chromatography of a variety of the simpler unsaturated esters have

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been extensively documented in data compilations^{7,8} and systematic studies relevant to this work have been previously reviewed⁹.

The present study extends the simple structure-retention trends observed in our previous work in terms of statistically determined increments for the structural parameters present in the series of unsaturated esters examined. A more comprehensive range of compounds and stationary phases is evaluated than previously employed to provide carefully prepared data for further study of the substance polarity factors of Rohrschneider.

EXPERIMENTAL

Gas chromatography

Chromatography was carried out on a modified F & M 810/29 Research Chromatograph fitted with improved flow control and thermostatic column-oven controller. The oven temperature was independently monitored throughout the determinations with a calibrated thermocouple. The retention data were obtained isothermally at 150° using 12 ft. × $\frac{1}{4}$ in. O.D. aluminium columns packed with 10% stationary phase on 62-72 mesh acid-washed and silanized Celatom. Flame ionization detection was used with the following conditions: injection temperature, 190°; detector temperature, 220°; carrier gas, helium; flow-rate, 30 ml/min with an inlet pressure of 45 p.s.i.

Stationary phases

The stationary phases used were all polysiloxanes and could be separated into three basic classes depending on the type of substituent group. Class I consisted of non-polar phases, primarily containing alkyl groups, class II of the low- to medium-polarity donor phases, containing groups capable of exhibiting donor properties, and class III of the medium to polar acceptor phases, which contained substituents exhibiting acceptor properties.

The degree and type of substitution, as well as the classification of polarity in terms of Rohrschneider constants, for the polysiloxanes have been shown⁹.

Low-molecular-weight polydiphenylsiloxane oligomers were prepared by conventional synthesis; diphenyldichlorosilane containing less than 1% triphenylchlorosilane as chain terminator was hydrolyzed by slowly dropping it into a 10% sodium carbonate solution. A reaction temperature of 25° was maintained to minimize any preliminary polymerization while the hydrogen chloride evolved was neutralized and the solid di- and triphenylsilanols formed were broken up.

The dry silanol mixtures were polymerized by heating a solution in toluene containing potassium hydroxide. The reaction was continued until water liberation ceased and further toluene was added to dissolve the low-molecular-weight products while the higher-molecular-weight species were essentially insoluble at room temperature. The soluble material was neutralized, freed of water and toluene and recovered as a white solid.

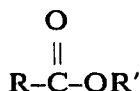
Preparation of esters

The esters were largely of commercial quality and of substantial purity. Esters prepared in the laboratory employed conventional esterification or transesterifi-

cation procedures using the macroreticular acidic ion exchanger Amberlyst 15 (Rohm & Haas, Philadelphia, Pa., U.S.A.).

RESULTS AND DISCUSSION

The retention data of the esters examined are shown in Tables I and II as relative retention, V_R , using *n*-nonane as standard and as retention indices, I . The esters are conveniently represented as:



where R and R' are the number of carbon atoms in the acid and alcohol chains, respectively. The effect of unsaturation in the acid chain R, on retention is shown in Fig. 1 for four stationary phases, *i.e.*, SE-30, polydiphenylsiloxane (100% Phenyl), DC-530 and Silar 5CP, while the deviations due to unsaturation with respect to the corresponding saturated esters⁹ are shown in Table III for all of the stationary phases considered.

The plots in Fig. 1 show considerable variation in relative retention, although three of the ester series are isomeric, differing in branching and position of unsaturation. Examination of boiling-point differences shows that the retention behaviour exhibited in Table III and Fig. 1 for non-polar phases is, as expected, closely related to boiling point. An important feature of the boiling-point differences of the ethyl esters is that the 2-butenate ester (the *trans* isomer or crotonate ester) and the 3-methyl 2-butenate ester exhibit an increase in boiling point of approximately 25° when compared to their saturated homologs, *i.e.*, ethyl butyrate and ethyl isopentanoate. While it would be expected that these unsaturated esters exhibit a slight change in dipole moment due to the combined effects of the weakly donor methyl-branched groups and loss of rotation due to the position of the unsaturation, the large increase in boiling point is unexpected. From a study of molecular models, it was apparent that the boiling points were affected by the shape of the molecules and steric hindrance of the carbonyl group. The 2-propenoic, 3-butenic, 2-methyl-2-propenoic and the *cis*-2-butenic acid esters were either compact molecules or capable of forming compact molecules due to rotation around the single bond in the acid chain. This would result in these substances having similar boiling points to their saturated homologs. The 2-methyl-2-propenates exhibited slightly higher boiling points (8°), but due to the position of unsaturation in the acid chain, are less likely to form as compact a side chain, nor will this acid chain shield the carbonyl group to the extent of the saturated ester, *i.e.*, the isobutyrate esters. The *trans*-2-butenate and 3-methyl-2-butenate ester series exhibited a similar basic structure, and were the only series of esters where the rotation of the acid chain did not significantly affect the shape of the molecule or sterically hinder the carbonyl group to the extent of their saturated homologs, hence their higher boiling points.

It is apparent from Fig. 1 that as the polarity of the stationary phase increased, the separation (or intercept) of the series changed, such that the retention volumes of the 2-propenoate, 2-butenate and 3-butenate ester series increased with respect to that of the 2-methyl-2-propenoate and the 3-methyl-2-butenate series. This effect

TABLE I
RETENTION DATA FOR UNSATURATED ESTERS ON NON-POLAR AND DONOR STATIONARY PHASES

Compounds	SE-30		OV-7		DC-710		OV-25		100% Phenyl		DC-230		DC-530	
	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I
Methyl 2-propenoate	0.202	603	0.255	657	0.312	693	0.506	777	0.681	829	0.219	625	0.335	688
Ethyl 2-propenoate	0.313	684	0.401	739	0.513	782	0.705	836	0.952	893	0.321	695	0.469	753
Propyl 2-propenoate	0.537	783	0.720	844	0.889	881	1.256	944	1.553	987	0.564	797	0.742	843
Butyl 2-propenoate	0.901	878	1.250	944	1.554	981	2.081	1037	2.684	1091	0.993	899	1.207	937
Pentyl 2-propenoate	1.511	973	2.154	1042	2.675	1078	3.456	1131	4.386	1185	1.718	998	2.007	1036
Hexyl 2-propenoate	2.518	1066	3.654	1137	4.527	1173	5.644	1221	7.053	1276	2.940	1096	3.280	1132
Isopropyl 2-propenoate	0.395	727	0.510	782	0.593	808	0.785	857	1.026	908	0.412	740	0.553	786
Isobutyl 2-propenoate	0.732	840	0.979	900	1.182	932	1.588	987	2.026	1038	0.794	859	0.989	899
Isopentyl 2-propenoate	1.265	940	1.765	1006	2.111	1036	2.763	1089	3.553	1145	1.423	964	1.681	1002
Methyl 2-methyl-2-propenoate	0.338	699	0.428	751	0.544	793	0.794	860	1.054	913	0.342	706	0.464	751
Ethyl 2-methyl-2-propenoate	0.500	770	0.654	827	0.789	860	1.106	921	1.432	971	0.510	778	0.656	819
Propyl 2-methyl-2-propenoate	0.832	863	1.133	926	1.373	959	1.844	1015	2.297	1062	0.904	882	1.084	917
Butyl 2-methyl-2-propenoate	1.409	960	1.925	1021	2.383	1058	3.063	1108	3.864	1161	1.560	981	1.770	1012
Pentyl 2-methyl-2-propenoate	2.328	1052	3.271	1117	4.034	1152	5.013	1199	6.243	1252	2.662	1078	2.880	1107
Hexyl 2-methyl-2-propenoate	3.849	1144	5.497	1210	6.772	1245	8.119	1288	9.973	1342	4.514	1173	4.683	1201
Isopropyl 2-methyl-2-propenoate	0.612	807	0.770	856	0.926	888	1.175	932	1.541	985	0.613	812	0.809	859
Isobutyl 2-methyl-2-propenoate	1.150	923	1.527	980	1.832	1011	2.300	1056	2.892	1106	1.235	939	1.443	972
Isopentyl 2-methyl-2-propenoate	1.951	1020	2.681	1081	3.235	1113	3.994	1157	5.000	1210	2.177	1041	2.413	1072
Methyl 2-butenolate	0.457	753	0.652	826	0.859	875	1.231	940	1.845	1020	0.500	775	0.656	819
Ethyl 2-butenolate	0.679	826	0.990	902	1.262	944	1.788	1009	2.405	1070	0.743	847	0.931	887
Propyl 2-butenolate	1.149	922	1.689	998	2.211	1044	3.013	1105	3.946	1165	1.318	950	1.533	984
Butyl 2-butenolate	1.924	1017	2.894	1095	3.805	1142	4.994	1198	6.514	1261	2.275	1049	2.533	1082
Pentyl 2-butenolate	3.193	1110	4.901	1190	6.463	1237	8.200	1290	10.622	1354	3.919	1148	4.138	1177
Hexyl 2-butenolate	5.284	1202	8.248	1284	10.873	1332	13.369	1380	17.081	1445	6.604	1242	6.677	1271
Isopropyl 2-butenolate	0.834	864	1.202	937	1.530	978	1.806	1011	2.487	1076	0.923	886	1.114	922
Isobutyl 2-butenolate	1.529	975	2.261	1050	2.920	1094	3.794	1148	5.054	1212	1.800	1007	2.036	1039
Isopentyl 2-butenolate	2.622	1074	4.012	1154	5.195	1198	6.606	1250	8.595	1313	3.201	1111	3.449	1142

Methyl 3-butenolate	0.328	692	0.448	759	0.596	809	0.856	873	1.136	927	0.342	706	0.525	775
Ethyl 3-butenolate	0.500	770	0.675	833	0.870	877	1.206	937	1.591	991	0.518	781	0.751	845
Propyl 3-butenolate	0.828	862	1.163	931	1.480	972	1.986	1029	2.568	1083	0.905	882	1.266	947
Butyl 3-butenolate	1.384	957	1.994	1028	2.562	1071	3.269	1120	4.108	1173	1.568	982	2.120	1047
Pentyl 3-butenolate	2.287	1049	3.393	1124	4.325	1165	5.350	1211	6.730	1267	2.680	1079	3.313	1134
Hexyl 3-butenolate	3.796	1142	5.727	1218	7.264	1258	8.681	1300	10.649	1354	4.563	1175	5.421	1230
Isopropyl 3-butenolate	0.613	806	0.825	869	1.027	907	1.338	956	1.730	1007	0.640	820	0.958	892
Isobutyl 3-butenolate	1.135	920	1.571	985	1.969	1024	2.481	1070	3.108	1119	1.261	942	1.692	1003
Isopentyl 3-butenolate	1.912	1016	2.752	1086	3.473	1125	4.263	1169	5.279	1220	2.214	1044	2.821	1103
Methyl 3-methyl-2-butenolate	0.698	831	1.012	906	1.346	955	1.875	1018	2.487	1077	0.779	855	0.975	896
Ethyl 3-methyl-2-butenolate	1.028	902	1.512	978	1.997	1026	2.744	1088	3.534	1144	1.243	940	1.384	964
Propyl 3-methyl-2-butenolate	1.710	995	2.574	1074	3.387	1121	4.456	1177	5.622	1232	2.014	1027	2.230	1057
Butyl 3-methyl-2-butenolate	2.834	1088	4.399	1170	5.784	1217	7.369	1270	9.081	1324	3.437	1124	3.360	1153
Pentyl 3-methyl-2-butenolate	4.661	1179	7.445	1265	9.815	1312	12.138	1362	14.730	1416	5.887	1222	5.912	1247
Hexyl 3-methyl-2-butenolate	7.661	1271	12.534	1359	16.473	1405	19.730	1452	23.487	1505	9.955	1317	9.535	1340
Isopropyl 3-methyl-2-butenolate	1.261	940	1.638	992	2.329	1054	3.106	1111	3.946	1165	1.417	964	1.620	995
Isobutyl 3-methyl-2-butenolate	2.306	1050	3.436	1126	4.435	1169	5.613	1220	6.946	1273	2.739	1083	2.921	1110
Isopentyl 3-methyl-2-butenolate	3.880	1146	6.043	1228	7.950	1274	9.619	1319	11.703	1372	4.806	1185	4.881	1210
<i>trans</i> -2-Hexenyl formate	1.040	904	1.521	979	1.909	1018	2.449	1067	3.000	1113	1.195	933	1.617	994
<i>trans</i> -2-Hexenyl acetate	1.595	983	2.449	1065	3.135	1107	4.160	1165	5.205	1218	1.862	1013	2.154	1050
<i>trans</i> -2-Hexenyl propionate	2.573	1070	3.952	1151	5.088	1194	6.571	1249	7.846	1296	3.050	1102	3.270	1132
<i>trans</i> -2-Hexenyl butyrate	4.034	1153	6.276	1234	8.057	1276	9.981	1326	11.692	1372	4.896	1182	5.000	1214

(Continued on p. 176)

TABLE I (continued)

Compounds	Stationary phase													
	SE-30		OV-7		DC-710		OV-25		100% Phenyl		DC-230		DC-530	
	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I
<i>trans</i> -2-Hexenyl pentanoate	6.583	1243	10.518	1327	13.647	1371	16.455	1418	18.846	1463	8.222	1282	8.050	1307
<i>trans</i> -2-Hexenyl hexanoate	10.981	1337	17.570	1420	22.838	1463	26.455	1506	30.026	1552	13.745	1375	12.868	1398
<i>cis</i> -2-Hexenyl formate	1.031	903	1.449	970	1.869	1014	2.459	1068	2.795	1099	1.153	926	1.534	984
<i>cis</i> -2-Hexenyl acetate	1.587	982	2.342	1057	3.020	1100	3.974	1156	4.846	1204	1.796	1007	2.091	1044
<i>cis</i> -2-Hexenyl propionate	2.557	1069	3.773	1143	4.899	1187	6.321	1242	7.487	1287	2.942	1096	3.214	1128
<i>cis</i> -2-Hexenyl butyrate	4.006	1152	5.970	1225	7.727	1269	9.583	1319	11.092	1362	4.716	1181	4.918	1211
<i>cis</i> -2-Hexenyl pentanoate	6.575	1243	10.055	1319	13.040	1363	15.756	1410	18.282	1458	7.938	1276	7.925	1304
<i>cis</i> -2-Hexenyl hexanoate	10.767	1333	16.752	1411	21.828	1455	25.500	1499	28.308	1541	13.231	1368	12.679	1395
<i>trans</i> -3-Hexenyl formate	1.006	898	1.436	969	1.838	1011	2.321	1057	2.846	1102	1.127	922	1.510	981
<i>trans</i> -3-Hexenyl acetate	1.527	975	2.242	1049	2.855	1090	3.794	1148	4.744	1200	1.769	1004	1.934	1029
<i>trans</i> -3-Hexenyl propionate	2.477	1063	3.660	1137	4.677	1179	5.987	1232	7.359	1284	2.840	1090	3.120	1122
<i>trans</i> -3-Hexenyl butyrate	3.887	1146	5.795	1220	7.428	1262	9.218	1311	11.795	1374	4.840	1186	4.975	1213
<i>trans</i> -3-Hexenyl pentanoate	6.383	1237	9.767	1314	12.522	1355	15.090	1402	17.692	1451	7.665	1269	7.711	1299
<i>trans</i> -3-Hexenyl hexanoate	10.393	1327	15.999	1403	20.926	1448	24.410	1491	27.897	1538	12.889	1364	12.208	1388
<i>cis</i> -3-Hexenyl formate	1.036	903	1.479	974	1.872	1015	2.474	1069	2.949	1109	1.160	927	1.522	983
<i>cis</i> -3-Hexenyl acetate	1.552	978	2.267	1051	2.960	1097	3.808	1148	4.974	1209	1.791	1006	2.069	1042
<i>cis</i> -3-Hexenyl propionate	2.575	1071	3.773	1143	4.798	1183	6.199	1238	7.462	1286	2.936	1096	3.230	1129
<i>cis</i> -3-Hexenyl butyrate	4.050	1154	5.988	1226	7.593	1266	9.449	1316	11.128	1363	4.698	1181	4.909	1211
<i>cis</i> -3-Hexenyl pentanoate	6.600	1243	9.976	1318	12.811	1360	15.430	1406	17.897	1453	7.902	1275	7.899	1303
<i>cis</i> -3-Hexenyl hexanoate	10.735	1333	16.540	1409	21.357	1451	24.885	1494	28.923	1545	13.195	1368	12.554	1393
Pent-1-ene-3-yl acetate	0.626	812	0.846	873	1.040	909	1.319	953	1.619	995	0.656	824	0.840	867
Hex-1-ene-3-yl acetate	0.974	897	1.418	966	1.687	996	2.131	1041	2.547	1081	1.079	914	1.337	957
Hept-1-ene-3-yl acetate	1.575	989	2.279	1052	2.838	1089	3.469	1131	3.976	1166	1.819	1009	2.126	1048
Oct-1-ene-3-yl acetate	2.580	1083	3.803	1144	4.697	1180	5.556	1218	6.381	1257	3.007	1100	3.315	1134
Non-1-ene-3-yl acetate	4.165	1175	6.373	1237	7.916	1273	8.900	1305	10.191	1346	5.023	1193	5.330	1227
Dec-1-ene-3-yl acetate	6.730	1267	10.676	1330	13.276	1366	14.220	1391	16.429	1437	8.448	1287	8.654	1321

TABLE II
RETENTION DATA FOR UNSATURATED ESTERS ON ACCEPTOR STATIONARY PHASES

Compounds	Stationary phase													
	XE-60		XF-1150		OV-225		Silvar 5CP		F-400		F-500		QF-1	
	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I
Methyl 2-propenoate	0.710	829	1.477	989	0.767	850	1.304	952	0.345	692	0.448	743	0.860	869
Ethyl 2-propenoate	1.005	903	2.000	1053	1.069	918	1.760	1014	0.526	775	0.670	823	1.172	939
Propyl 2-propenoate	1.635	1006	3.012	1140	1.785	1024	2.810	1112	0.889	878	1.138	926	1.788	1036
Butyl 2-propenoate	2.615	1106	4.581	1229	2.888	1123	4.468	1209	1.488	979	1.887	1025	2.761	1135
Pentyl 2-propenoate	4.145	1204	6.907	1316	4.672	1222	7.000	1302	2.470	1079	3.121	1124	4.257	1234
Hexyl 2-propenoate	6.530	1301	10.395	1402	7.431	1317	10.747	1392	4.066	1177	5.100	1220	6.451	1329
Isopropyl 2-propenoate	1.120	926	1.930	1046	1.190	941	1.873	1027	0.620	807	0.829	863	1.336	969
Isobutyl 2-propenoate	2.070	1056	3.616	1179	2.250	1071	3.380	1150	1.211	939	1.561	988	2.389	1102
Isopentyl 2-propenoate	3.420	1163	5.651	1273	3.810	1180	5.608	1256	2.100	1047	2.644	1091	3.735	1204
Methyl 2-methyl-2-propenoate	1.055	913	1.936	1046	1.172	937	1.861	1026	0.554	785	0.695	829	1.106	926
Ethyl 2-methyl-2-propenoate	1.415	975	2.510	1101	1.569	997	2.317	1072	0.798	857	1.017	904	1.504	996
Propyl 2-methyl-2-propenoate	2.250	1074	3.767	1187	2.517	1094	3.772	1173	1.345	959	1.686	1003	2.398	1103
Butyl 2-methyl-2-propenoate	3.580	1173	5.686	1274	4.043	1192	5.835	1264	2.223	1058	2.778	1100	3.717	1203
Pentyl 2-methyl-2-propenoate	5.585	1268	8.535	1360	6.414	1287	9.051	1356	3.655	1156	4.544	1197	5.602	1297
Hexyl 2-methyl-2-propenoate	8.735	1363	12.837	1447	10.121	1380	13.868	1445	5.972	1253	7.352	1292	8.451	1391
Isopropyl 2-methyl-2-propenoate	1.530	992	2.488	1099	1.647	1007	2.430	1082	0.965	894	1.226	940	1.795	1037
Isobutyl 2-methyl-2-propenoate	2.890	1127	4.593	1229	3.138	1140	4.494	1210	1.829	1020	2.310	1065	3.155	1166
Isopentyl 2-methyl-2-propenoate	4.755	1234	7.093	1327	5.225	1245	7.380	1313	3.098	1123	3.883	1167	4.996	1271
Methyl 2-butenolate	1.745	1020	3.372	1146	1.965	1044	3.253	1143	0.840	867	1.114	921	1.788	1036
Ethyl 2-butenolate	2.310	1080	4.244	1213	2.635	1104	4.266	1199	1.216	940	1.596	992	2.472	1110
Propyl 2-butenolate	3.660	1178	6.535	1304	4.252	1202	6.671	1292	2.050	1042	2.649	1092	3.850	1211
Butyl 2-butenolate	5.820	1276	9.837	1390	6.817	1299	10.468	1386	3.390	1141	4.376	1190	5.903	1309
Pentyl 2-butenolate	9.110	1372	14.767	1476	10.800	1394	16.291	1479	5.590	1240	7.180	1287	8.920	1403
Hexyl 2-butenolate	14.260	1467	22.070	1561	17.026	1487	24.848	1567	9.255	1339	11.678	1383	13.566	1499
Isopropyl 2-butenolate	2.360	1084	4.326	1217	2.678	1107	4.367	1204	1.477	978	1.948	1031	1.890	1045
Isobutyl 2-butenolate	4.660	1229	7.837	1342	5.304	1248	8.013	1337	2.749	1100	3.593	1151	5.248	1282
Isopentyl 2-butenolate	7.530	1331	12.221	1436	8.748	1351	13.114	1433	4.676	1204	6.030	1253	7.832	1373

(Continued on p. 178)

TABLE II (continued)

Compounds	Stationary phase													
	XE-60		XF-1150		OV-225		Silar SCP		F-400		F-500		QF-1	
	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I
Methyl 3-butenolate	1.250	949	2.465	1098	1.365	969	2.279	1068	0.568	790	0.738	841	1.221	949
Ethyl 3-butenolate	1.645	1008	3.023	1143	1.800	1026	2.962	1123	0.808	859	1.079	915	1.690	1023
Propyl 3-butenolate	2.590	1104	4.535	1227	2.904	1124	4.506	1210	1.373	963	1.754	1011	2.602	1122
Butyl 3-butenolate	4.055	1200	6.849	1314	4.583	1218	7.025	1303	2.275	1063	2.879	1108	3.991	1219
Pentyl 3-butenolate	6.375	1296	10.221	1399	7.252	1312	10.924	1395	3.732	1160	4.708	1204	6.106	1316
Hexyl 3-butenolate	9.955	1391	15.337	1484	11.478	1406	16.722	1482	6.094	1256	7.629	1299	9.301	1415
Isopropyl 3-butenolate	1.795	1026	3.012	1140	1.948	1042	3.000	1126	0.975	896	1.296	951	1.982	1059
Isobutyl 3-butenolate	3.280	1154	5.465	1266	3.574	1167	5.392	1248	1.889	1026	2.375	1072	3.443	1186
Isopentyl 3-butenolate	5.260	1255	8.442	1358	5.852	1268	8.785	1349	3.159	1127	3.988	1172	5.319	1285
Methyl 3-methyl-2-butenolate	2.315	1080	4.337	1217	2.670	1107	4.213	1196	1.146	928	1.571	989	2.186	1082
Ethyl 3-methyl-2-butenolate	3.095	1142	5.174	1254	3.590	1167	5.563	1254	1.711	1007	2.304	1064	2.938	1149
Propyl 3-methyl-2-butenolate	4.800	1235	7.907	1344	5.687	1262	8.563	1344	2.889	1110	3.708	1158	4.336	1238
Butyl 3-methyl-2-butenolate	7.500	1330	11.814	1429	9.026	1357	13.213	1435	4.749	1207	6.079	1255	6.611	1335
Pentyl 3-methyl-2-butenolate	11.730	1426	17.663	1514	14.296	1451	20.650	1522	7.794	1305	9.946	1351	10.159	1433
Hexyl 3-methyl-2-butenolate	18.250	1520	26.326	1599	22.313	1543	31.000	1613	12.645	1400	16.058	1445	15.292	1526
Isopropyl 3-methyl-2-butenolate	3.535	1170	5.233	1257	3.852	1182	5.688	1259	2.101	1047	2.696	1095	3.274	1174
Isobutyl 3-methyl-2-butenolate	5.970	1282	9.326	1379	7.017	1305	10.113	1379	3.861	1167	4.942	1202	5.735	1302
Isopentyl 3-methyl-2-butenolate	9.465	1380	14.419	1471	11.530	1407	16.288	1479	6.519	1270	8.313	1316	8.752	1399
<i>trans</i> -2-Hexenyl formate	3.950	1194	6.296	1296	4.080	1194	6.066	1273	1.768	1012	2.207	1058	3.272	1174
<i>trans</i> -2-Hexenyl acetate	4.948	1242	7.716	1340	5.431	1253	8.030	1331	2.761	1101	3.471	1145	4.579	1251
<i>trans</i> -2-Hexenyl propionate	6.859	1311	10.148	1397	7.948	1331	11.443	1405	4.253	1186	5.223	1225	6.132	1317

<i>trans</i> -2-Hexenyl butyrate	9.980	1391	14.046	1466	11.612	1409	16.180	1477	6.551	1271	7.915	1308	8.737	1398
<i>trans</i> -2-Hexenyl pentanoate	15.404	1484	20.830	1549	18.241	1502	24.677	1565	10.632	1367	12.893	1402	13.149	1492
<i>trans</i> -2-Hexenyl hexanoate	23.838	1577	30.898	1633	28.480	1593	34.431	1635	17.197	1460	20.736	1495	19.614	1583
<i>cis</i> -2-Hexenyl formate	3.598	1174	6.296	1296	3.836	1181	6.175	1276	1.695	1005	2.107	1047	3.211	1170
<i>cis</i> -2-Hexenyl acetate	4.668	1230	7.625	1337	5.285	1247	8.100	1333	2.649	1093	3.298	1135	4.474	1245
<i>cis</i> -2-Hexenyl propionate	6.784	1309	10.102	1396	7.733	1325	11.538	1407	4.081	1178	4.967	1215	5.974	1311
<i>cis</i> -2-Hexenyl butyrate	9.349	1377	14.046	1466	11.267	1403	16.288	1479	6.277	1262	7.554	1297	8.491	1392
<i>cis</i> -2-Hexenyl pentanoate	15.286	1482	20.921	1550	17.741	1496	24.950	1568	10.193	1358	12.223	1392	12.746	1485
<i>cis</i> -2-Hexenyl hexanoate	23.608	1575	30.875	1632	27.552	1586	37.700	1654	16.509	1452	19.620	1485	19.070	1577
<i>trans</i> -3-Hexenyl formate	3.500	1168	5.864	1281	3.785	1178	5.995	1270	1.663	1001	2.079	1044	3.123	1163
<i>trans</i> -3-Hexenyl acetate	4.495	1221	6.886	1315	4.983	1235	7.361	1313	2.547	1085	3.198	1128	4.430	1243
<i>trans</i> -3-Hexenyl propionate	6.540	1301	9.557	1384	7.362	1315	10.626	1389	3.972	1172	4.834	1210	6.061	1315
<i>trans</i> -3-Hexenyl butyrate	9.551	1382	13.318	1455	10.853	1395	15.169	1464	6.502	1269	7.934	1307	8.693	1397
<i>trans</i> -3-Hexenyl pentanoate	14.869	1476	19.852	1539	17.035	1488	23.241	1555	9.997	1354	12.058	1389	13.149	1492
<i>trans</i> -3-Hexenyl hexanoate	23.046	1569	29.443	1622	26.733	1580	34.699	1636	16.158	1448	19.355	1482	19.526	1582
<i>cis</i> -3-Hexenyl formate	3.632	1176	6.511	1303	3.931	1186	6.229	1278	1.702	1006	2.141	1050	3.254	1174
<i>cis</i> -3-Hexenyl acetate	4.813	1236	7.739	1340	5.285	1247	7.976	1330	2.642	1092	3.393	1140	4.658	1255
<i>cis</i> -3-Hexenyl propionate	6.929	1314	10.466	1404	7.759	1326	11.313	1403	4.067	1177	5.062	1219	6.211	1320
<i>cis</i> -3-Hexenyl butyrate	10.061	1393	14.466	1472	11.363	1404	15.988	1475	6.267	1262	7.595	1298	8.825	1401
<i>cis</i> -3-Hexenyl pentanoate	15.636	1487	21.489	1556	17.836	1497	24.494	1564	10.207	1358	12.252	1392	13.281	1494
<i>cis</i> -3-Hexenyl hexanoate	24.131	1579	31.761	1638	27.759	1588	37.072	1650	16.411	1451	19.607	1484	20.597	1594
Pent-1-ene-3-yl acetate	1.950	1044	2.784	1123	2.009	1048	3.138	1135	1.089	915	1.403	967	2.000	1061
Hex-1-ene-3-yl acetate	2.915	1129	4.182	1209	3.000	1131	4.725	1220	1.734	1002	2.152	1051	2.991	1153
Hept-1-ene-3-yl acetate	4.447	1219	6.410	1300	4.716	1224	7.013	1303	2.908	1093	3.354	1138	4.509	1247
Oct-1-ene-3-yl acetate	6.849	1311	9.705	1388	7.379	1316	10.363	1384	4.405	1177	5.276	1227	6.675	1337
Non-1-ene-3-yl acetate	10.633	1405	14.421	1471	11.560	1408	15.788	1472	7.270	1271	8.506	1321	9.904	1427
Dec-1-ene-3-yl acetate	16.422	1497	21.545	1556	18.052	1499	23.450	1555	11.809	1362	13.683	1414	14.904	1520

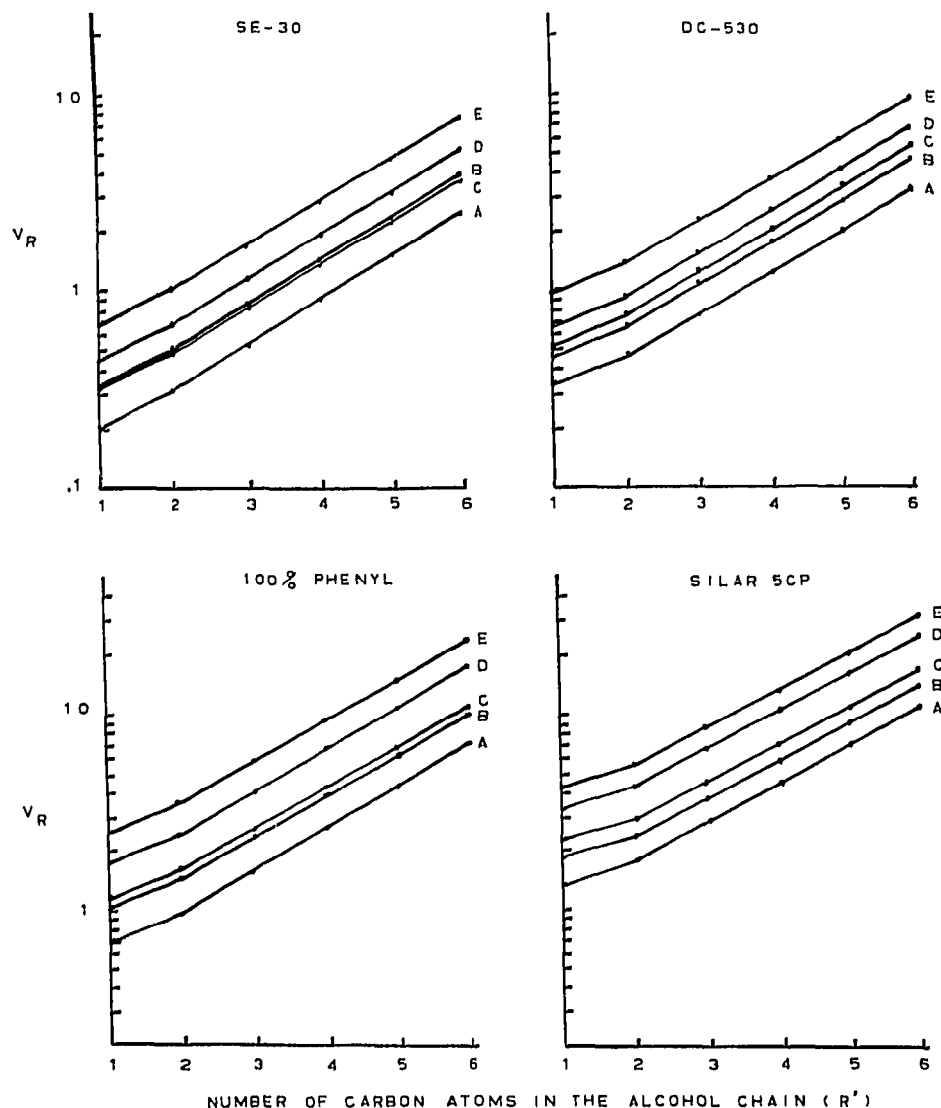


Fig. 1. Plots of logarithm of relative retention (V_R) versus the number of carbon atoms in the acid chain (R) of unsaturated esters. A, 2-propenoates; B, 2-methyl-2-propenoates; C, 1-butenates; D, 2-butenates; E, 3-methyl-2-butenates.

is due to isomerism in the acid chain and consequent screening of the carbonyl group which as reported previously⁹ was found to result in negative deviations from normal structures that increased with polarity of the stationary phase.

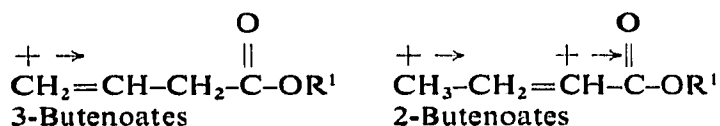
Table III shows a trend where the deviation between the unsaturated and saturated esters increased positively with the increased general polarity of the stationary phase. This behaviour was a result in part of the presence of the polarisable double bond which in all series, except the 3-butenate esters, was conjugated to the π -bond

TABLE III
EFFECT OF UNSATURATION IN ACID CHAIN

Stationary phase	Retention index difference of saturated and unsaturated ethyl esters				
	2-Propenoate (-0.6°)*	2-Methyl- 2-propenoate (8.0°)	2-Butenoate (25.0°)	3-Butenoate (1.0°)	3-Methyl- 2-butenoate (22.0°)
SE-30	-7.2	29.1	47.8	-12.2	66.4
OV-7	-5.3	34.6	59.5	-7.3	89.0
DC-710	-3.2	36.8	72.1	0.9	105.7
OV-25	4.0	46.3	83.6	6.2	121.6
100% Phenyl	17.0	69.9	111.4	25.9	143.5
DC-230	0.2	31.1	54.4	-12.5	81.8
DC-530	5.8	38.0	60.6	21.3	82.6
XE-60	2.9	41.4	89.2	13.9	107.1
XF-1150	25.9	58.5	111.4	35.4	127.7
OV-225	11.7	56.0	106.7	26.2	124.8
Silar 5CP	13.8	62.5	114.9	32.5	137.7
F-400	-4.7	29.8	70.7	-8.6	79.6
F-500	-3.0	34.7	75.5	-6.5	91.1
QF-1	2.1	14.3	70.8	14.7	59.4

* Values in parentheses are boiling-point differences between saturated and unsaturated ethyl esters¹⁵.

in the carbonyl group. This effect is known to be more polar than with conjugated systems¹⁰ due to the resultant increased polarisability, *i.e.*



Allen and Haken¹⁰ concluded that the dipole moment of esters is not as great as the degree of polarisability, and the dipole moment of esters is little influenced by unsaturation, although it increases the polarisability. While this is undoubtedly correct, it is very difficult to measure the effect of unsaturation entirely free of other interactions. The increments in Table III are measured relative to normal and branched-chain saturated esters of equivalent carbon number and structure. It is noteworthy that in many instances the structure of the saturated ester is quite different from the unsaturated one as is apparent when the isopentanoate structure is compared with the 3-methyl-2-butenoate structure where the carbonyl group in the saturated ester structure is liable to be more sterically hindered by the acid side chain than in the unsaturated ester. This effect is common to many of the other homologous series as the geometry of the molecule can be severely affected by the different bond angles that π -bonds introduce. Hence this increased polarisability observed in Table III may primarily be due to the increased polarisability of the π -bond, but may also be a result of a decrease in shielding of the carboxyl group by the acid side chain, as unsaturation can reduce the rotation and change the bond angles and structures usually exhibited by saturated esters. Branched-chain saturated esters have exhibited negative

TABLE IV
EFFECT OF POLARITY ON DEVIATIONS DUE TO UNSATURATION

Stationary phase	Retention index difference of saturated and unsaturated series				
	2-Propenoate	2-Methyl- 2-propenoate	2-Butenoate	3-Butenoate	3-Methyl- 2-butenoate
OV-17	4.0	7.7	24.3	13.1	39.3
DC-530	13.0	8.9	12.8	33.5	16.2
OV-25	11.2	17.2	35.8	18.4	55.2
100% Phenyl	24.2	40.8	63.6	38.1	77.1
XE-60	10.1	12.3	41.4	26.1	40.7
XF-1150	33.1	29.4	63.6	47.6	61.3
Silar 5CP	21.0	33.4	67.1	44.7	71.3

deviations that increased with polarity, compared to less sterically hindered molecules⁹.

The magnitude of the deviations due to unsaturation on the polar donor and acceptor phases are shown in Table IV where the two most polar acceptor phases Silar 5CP and XF-1150 show the greatest deviation. This deviation, however, is only just greater than that with 100% Phenyl which exhibits only half the general polarity⁹ as compared to XF-1150. Similarly on OV-25 the deviation exhibited is comparable with XE-60, OV-25 being considerably less polar. This trend is not observed with the donor DC-530 phase, which is slightly less polar than OV-25 but more polar than OV-17, as in general the deviations obtained with DC-530 are similar or lower than those obtained with OV-17 (the 3-butenoate esters are the exception). The increased deviations found with donor phenyl phases, may be a result of an increased π -bond

TABLE V
EFFECT OF DEVIATIONS DUE TO METHYL, ISOPROPYL, ISOBUTYL AND ISOPENTYL STRUCTURES

Stationary phase	Retention index difference							
	Methyl average		Isopropyl average		Isobutyl average		Isopentyl average	
	Unsat.	Overall	Unsat.	Overall	Unsat.	Overall	Unsat.	Overall
SE-30	19.2	19.9	-56.2	-55.6	-36.8	-36.2	-32.0	-31.8
OV-7	20.8	21.9	-64.9	-65.4	-43.4	-43.4	-35.2	-36.6
DC-710	24.4	24.7	-68.4	-69.1	-47.8	-46.4	-39.6	-40.2
OV-25	28.0	27.5	-80.6	-74.4	-50.4	-46.1	-45.0	-40.2
100% Phenyl	34.0	34.0	-77.6	-66.6	-52.4	-52.0	-42.8	-42.9
DC-230	24.2	23.2	-63.2	-63.6	-41.0	-40.9	-36.8	-37.7
DC-530	27.8	26.5	-59.2	-62.4	-41.6	-38.7	-34.6	-31.5
XE-60	33.4	31.6	-79.8	-80.4	-48.2	-45.6	-41.2	-40.0
XF-1150	23.6	35.9	-88.6	-86.1	-52.2	-46.4	-41.2	-40.9
OV-225	35.4	35.5	-85.4	-85.4	-51.6	-48.9	-43.4	-43.3
Silar 5CP	37.2	38.4	-86.6	-88.4	-55.8	-53.5	-44.8	-44.9
F-400	24.0	25.1	-66.0	-62.4	-39.0	-38.1	-33.8	-34.6
F-500	22.8	25.5	-62.0	-61.2	-40.0	-38.1	-32.8	-33.5
QF-1	26.6	22.6	-65.0	-62.8	-32.6	-31.1	-30.2	-30.2

interaction between the phenyl group attached to the stationary phase and the double bond present in the acid chain of the ester.

Of the unsaturated ester deviations shown in Table III, two series exhibit increased deviation with respect to the other series on most phases, *i.e.*, the 2-butenate and 3-methyl-2-butenate ester series. This behaviour apparently is related to the specific rotations in the acid chain of these esters and consequent reduction in steric hindrance. This as previously discussed, resulted in an elevation in the boiling points of these ester series when compared to their saturated homologs and as demonstrated here, makes these esters more susceptible to polar interactions^{9,11}.

Methyl ester deviations are still apparent from Fig. 1 where no apparent trends could be observed between different series of unsaturated esters. In Table V the average deviations are shown for unsaturated esters in addition to the overall average methyl deviation on each stationary phase for all acid ester series, both saturated and unsaturated with deviations due to the isopropyl, isobutyl and isopentyl structures in the alcohol chain. Plots of this behaviour were essentially similar to that of the saturated esters⁹ and while variations occur between the unsaturated values and the overall average deviation, a definite trend was not apparent to indicate a change in polarisability in the alcohol chain due to unsaturation in the acid chain.

Fig. 1 shows that as the polarity of the stationary phase increases, especially on acceptor phases, *i.e.*, Silar 5CP, the slope or incremental change of the ester plots decreases. This is consistent with the behaviour of the saturated esters⁹ and consequently is related to the polarisability of the esters on the stationary phases. The increments based on ΔI are shown relative to the hydrocarbon plot in Table VI. As this hydrocarbon slope was observed to decrease with increased polarity of the stationary phase¹², these increments for the alcohol chain of unsaturated acid esters do not decrease with increased polarity unless the slope of the V_R plot is less than that of the hydrocarbon plot, which only occurs on the more polar phases, *i.e.*, XF-1150.

TABLE VI
INCREMENTAL RETENTION INDEX INCREASES ON HOMOLOGOUS
UNSATURATED ACID ESTERS

Stationary phase	Ester series				
	2-Propenoate	2-Methyl-2-propenoate	2-Butenoate	3-Butenoate	3-Methyl-2-butenate
SE-30	96.2	94.3	94.7	93.2	92.4
OV-7	100.9	96.5	96.1	97.0	95.7
DC-710	98.8	97.5	97.7	96.3	95.4
OV-25	97.8	92.7	93.6	91.3	91.5
100% Phenyl	98.0	94.2	94.8	91.8	90.8
DC-230	101.1	99.9	100.2	99.4	94.3
DC-530	94.3	95.9	96.8	96.7	94.5
XE-60	100.4	97.8	97.0	96.0	94.7
XF-1150	86.3	86.4	87.5	85.5	86.5
OV-225	101.7	96.8	96.7	95.2	94.7
Silar 5CP	96.2	94.3	93.4	90.9	89.5
F-400	101.3	99.6	99.9	100.3	99.1
F-500	100.5	97.6	98.4	96.4	95.8
QF-1	98.4	100.3	97.0	97.6	94.9

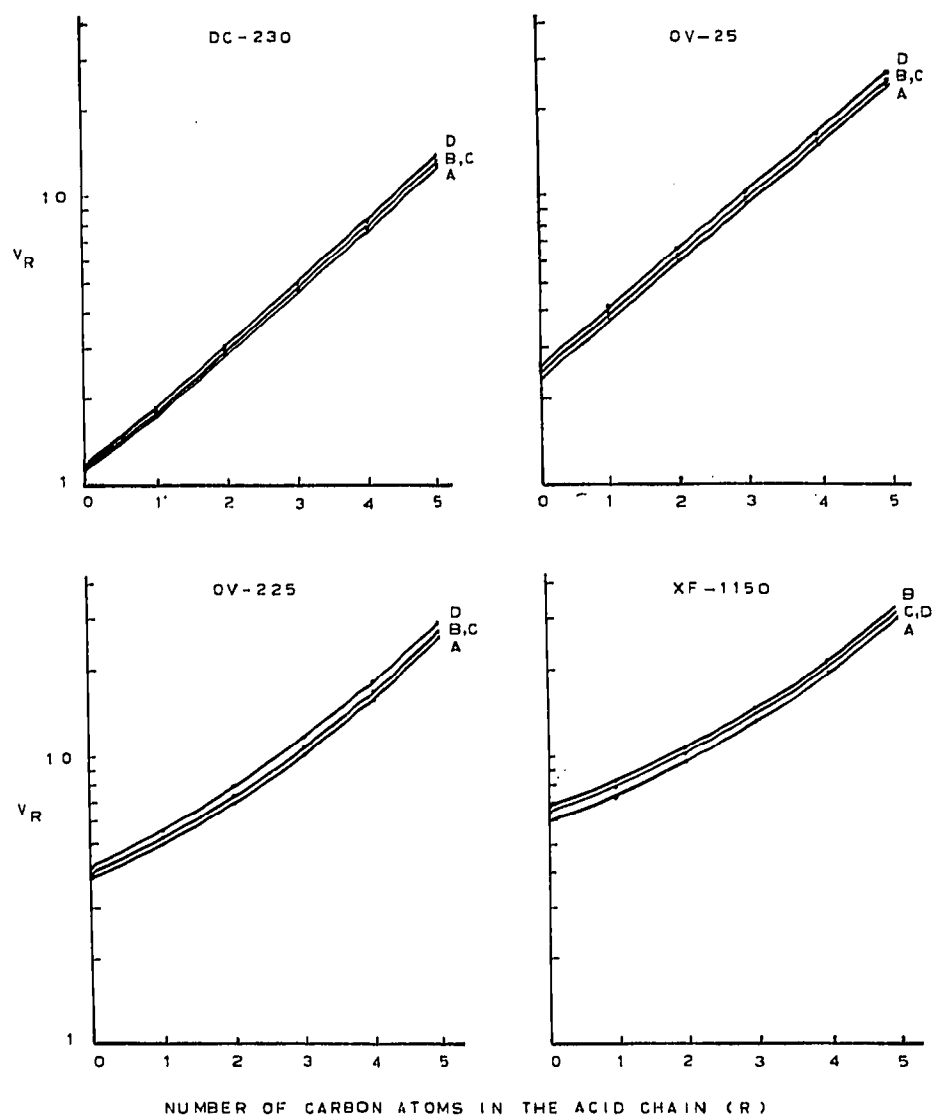


Fig. 2. Plots of logarithm of relative retention (V_R) versus the number of carbon atoms in the alcohol chain (R') of unsaturated esters. A, *trans*-3-hexenyl; B, *cis*-3-hexenyl; C, *cis*-2-hexenyl; D, *trans*-2-hexenyl.

This behaviour was also observed for increments in the alcohol chain of saturated esters⁹. A comparison of the increments of saturated and unsaturated esters was inconclusive, as no apparent trend was evident when the increments for similar structure and carbon number in the acid chains were compared. It is generally apparent from Table V, that the smallest increment occurred with the unsaturated ester series exhibiting the greater retention or intercept with the y -axis in comparison to the series exhibiting the lowest, *i.e.*, the 3-methyl-2-butenates had the smallest increment and

the 2-propenoates the highest, while the other unsaturated series were in between these, depending on the retention position, or intercept with the y -axis.

The effect of unsaturation in the alcohol chain, R' , is shown in Fig. 2 where V_R is plotted against R' for *cis*- and *trans*-2- and -3-hexenyl esters on DC-230, OV-25, OV-225 and XF-1150 stationary phases. The deviations due to the effect of unsaturation in these esters when compared to hexanoate esters are shown in Table VI for all stationary phases. On a non-polar graphitised carbon phase it was found that the *cis* isomer was eluted first for olefins¹³, unlike the behaviour of the geometric unsaturated esters here, which on non-polar phases followed that of the boiling points of the alcohols, *i.e.*, the *trans*-3 esters were eluted before the *cis*-3 esters (b.p. of alcohols 153° and 156°, respectively) followed by the *cis*-2-esters and finally the *trans*-3-esters (b.p. of alcohols 156.0° and 157.5°, respectively). From Fig. 2, on non-polar DC-230 there is little separation between the *cis*-3-, *cis*-2- and *trans*-3-esters which is consistent with the similarity in boiling-point behaviour of their alcohols. While the boiling points of alcohols are not always a true guide to the retention behaviour of their esters, the boiling points of these esters could not be determined accurately due to the micro-method of preparation of the ester series and thus a comparison of the alcohol boiling points was included, which in this case is apparently consistent with the ester retention behaviour. As the polarity of the phase increases the elution order changes, *i.e.*, on the most polar phase XF-1150 the elution order in order of increasing retention is: *trans*-3-, *cis*-2-, *trans*-2- and *cis*-3-hexenyl esters. However, with the second most polar phase, Silar 5CP, the order is slightly different, *i.e.*, *trans*-3-, *trans*-2-, *cis*-3- and *cis*-2-hexenyl esters. No definite trend is apparent when the elution on all phases is considered, as the retention volumes of these ester series were relatively close to each other, hence minor fluctuations in operating conditions would affect the elution order. It appears that the *cis* isomers were affected by polarity changes to a greater extent than the *trans* isomers as demonstrated by the elution orders above.

From studies on fatty acids, it would have been expected that the elution order would be affected by the position of unsaturation, as it is well known¹⁴ that as unsaturation approaches the extremities of the molecule, or the polar group in the molecule, the retention of the molecule is increased. This trend was present in the hexenyl ester series studied here, as the 2-position isomers generally were eluted after the 3-position isomers especially on the lower-polarity stationary phases. On polar phases *i.e.* QF-1, this trend was not always observed, and fatty-acid studies should not be used as a guide to the retention behaviour of simple esters, as polar interactions within the molecule in the latter systems are common, influencing retention more than in long-chain fatty acids and their esters, where intermolecular interactions are less prevalent.

It is interesting to compare the relative magnitudes of the deviations due to unsaturation in the alcohol chain as presented in Table VII. On non-polar and low-polarity phases, *i.e.*, SE-30, DC-230, F-400, etc., the deviations are, as expected, negative, and similarly as the polarity of the stationary phases increases the deviations become positive. The magnitude of these deviations was not as expected, *i.e.*, greatest deviation for the most polar phase, but they were similar to those found for unsaturation in the acid chain⁹. The greatest deviations are found with phases containing donor phenyl substituent groups, in spite of the fact that the most polar of these phases, 100% Phenyl, exhibits only half the general polarity of the most polar ac-

TABLE VII

DEVIATIONS DUE TO UNSATURATION IN THE ALCOHOL CHAIN

Stationary phase	Retention index difference of hexenyl ester series			
	<i>trans</i> -2	<i>cis</i> -2	<i>trans</i> -3	<i>cis</i> -3
SE-30	- 3.2	- 4.5	-10.5	- 4.5
OV-7	7.3	1.2	6.7	1.8
DC-710	17.2	10.8	3.2	7.7
OV-25	32.0	25.8	17.0	22.0
100% Phenyl	38.0	27.5	27.2	29.8
DC-230	0.0	- 6.5	- 9.7	- 6.7
DC-530	6.5	1.7	- 4.0	0.8
XE-60	17.0	7.5	2.5	13.8
XF-1150	19.7	19.0	5.5	25.0
OV-225	24.2	16.8	8.1	18.5
Silar 5CP	22.8	28.3	13.0	25.2
F-400	1.17	- 8.8	-10.7	- 6.8
F-500	3.83	- 4.3	- 7.5	- 4.7
QF-1	-21.5	-27.3	-25.3	-17.7

ceptor phase, XF-1150. This trend cannot be due to the presence of donor groups, as DC-710 exhibited deviations that were three times greater than those determined on DC-530, a non-phenyl donor substituted phase of equivalent general polarity. This behaviour as previously discussed⁹ is probably a result of increased polarisation due to a π -bond interaction between the unsaturation present in both the ester chain and the phenyl group of the stationary phases. Confirmation of this behaviour is demonstrated by the fact that both OV-225 and Silar 5CP stationary phases, containing both acceptor and donor phenyl groups, exhibit greater deviations than obtained on either XE-60 or XF-1150, which are phases containing identical proportions of the same acceptor groups. From Fig. 2 it is also apparent that as the polarity of the stationary phase increases, the linearity of these plots decreases, and the plots become curvi-linear. This effect is consistent with the trends reported previously with plots of the saturated alcohol ester series. For this reason the increments in the acid chain of the unsaturated alcohol ester series are not included.

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NOTE ADDED IN PROOF

Since submission of this work Silar 5CP has been re-named and is now available as APOLAR 5CP (Applied Science Labs. 1975 catalogue) and as AS 1 (ref. 16).

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