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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

VIII*. REDUCED RETENTION OF *n*- AND ISOALKYL PIVALATE ESTERS

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SUMMARY

Reduced retention of branched-chain esters due to screening of the carboxyl group is reported by considering the retention behaviour of the *n*- and isoalkyl esters of pivalic and pentanoic acids on polysiloxane stationary phases of varying polar character.

INTRODUCTION

Many workers have investigated the relationship between gas chromatographic retention and the chemical structures of the solute and solvent. Some empirical rules concerning retention with both polar and non-polar solvents and solutes have been known since the earliest works and although they have been refined to include the interactions of donor and acceptor groups in both species, these considerations would appear to be of limited general application. Elution of non-polar compounds according to boiling point or molecular weight on non-polar substrates has been extended to a study of simple esters¹⁻³ from which it is apparent that the compounds are frequently eluted substantially following boiling point, which is influenced by the shape of the molecule and the resultant steric hindrance. With substances that are hindered, some screening of the interactive group can occur and the increased retention anticipated with the use of more polar phases is not as significant.

The present work considers the concept of screening by a study of the effect of stationary phases of increasing polar character on the retention behaviours of the *n*-alkyl pivalates, where the carbonyl group is adjacent to a *tert.*-butyl group, and of the

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TABLE I
RETENTION DATA FOR NORMAL AND ISOMERIC SATURATED ESTERS AND STANDARD SUBSTANCES ON NON-POLAR AND
DONOR PHASES

Compound	Stationary phase											
	SE-30		OV-7		DC-710		100% Phenyl		DC-230		DC-530	
	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I
Benzene	0.296	674	0.360	719	0.471	767	0.800	860	0.309	688	0.423	733
Butanol	0.252	644	0.335	706	0.452	760	0.857	869	0.268	683	0.692	829
2-Pentanone	0.296	674	0.417	746	0.545	793	1.075	917	0.321	701	0.787	854
Nitropropane	0.378	718	0.671	832	0.946	892	1.825	1018	0.473	771	0.692	829
Pyridine	0.448	750	0.807	865	1.115	922	2.857	1117	0.599	809	0.754	846
2-Methyl-2-pentanol	0.386	722	0.496	777	0.566	800	0.905	881	0.304	685	0.740	842
<i>tert.</i> -Butyl acetate	0.317	686	0.384	731	0.455	761	0.692	833	0.420	743	0.414	729
Methyl pentanoate	0.611	807	0.837	871	1.027	907	1.675	1001	0.646	821	0.822	863
Ethyl pentanoate	0.894	876	1.230	941	1.498	975	2.273	1060	0.976	896	1.163	930
Propyl pentanoate	1.499	971	2.082	1036	2.529	1069	3.591	1147	1.675	994	1.872	1023
Butyl pentanoate	2.472	1063	3.508	1130	4.283	1163	5.773	1237	2.840	1089	3.021	1116
Pentyl pentanoate	4.039	1155	5.807	1222	7.216	1257	9.318	1329	4.801	1185	4.890	1210
Hexyl pentanoate	6.719	1247	9.900	1316	12.057	1349	15.023	1420	8.057	1287	7.920	1304
Isopropyl pentanoate	1.106	915	1.453	971	1.724	1000	2.523	1079	1.191	932	1.365	961
Isobutyl pentanoate	2.028	1027	2.776	1087	3.317	1117	4.432	1187	2.297	1051	2.472	1077
Isopentyl pentanoate	3.600	1132	4.776	1185	5.774	1217	7.455	1286	3.957	1150	4.056	1173
Methyl pivalate	0.368	706	0.436	749	0.498	783	0.806	860	0.356	721	0.452	751
Ethyl pivalate	0.512	771	0.600	809	0.692	842	0.935	899	0.509	785	0.622	814
Propyl pivalate	0.849	870	1.046	913	1.194	939	1.581	994	0.873	881	1.032	914
Butyl pivalate	1.374	965	1.741	1008	2.004	1031	2.484	1084	1.491	976	1.661	1008
Pentyl pivalate	2.236	1061	2.895	1103	3.379	1124	4.097	1184	2.516	1069	2.671	1102
Hexyl pivalate	—	—	—	—	—	—	6.484	1276	—	—	—	—
Isopropyl pivalate	0.621	809	0.711	841	0.780	863	0.871	875	0.604	815	0.707	839
Isobutyl pivalate	1.182	936	1.426	971	1.617	993	1.903	1031	1.251	945	1.378	971
Isopentyl pivalate	1.904	1030	2.384	1067	2.753	1087	3.258	1139	2.109	1038	2.226	1066

isoalkyl esters, where chain branching also occurs adjacent to the carboxyl oxygen atom.

Limited retention data of the methyl^{4,5} and ethyl esters⁶ have been reported while the most extensive work by Eidus and co-workers⁷ showed retention plots of the α,α -dimethylalkanoic acids and of their isobutyl esters on a polar column containing 18% DEGS and 4% phosphoric acid. Plots were also shown of the α -alkanoic, the α -ethylalkanoic acids and of the isobutyl esters. The retention of the acids and esters of the α,α -dimethylalkanes $<$ α -methylalkanes $<$ α -ethylalkanes while the first member of the dimethyl series on both plots, *i.e.* pivalic acid and isobutyl pivalate, showed substantially reduced retention as compared with the other members of the series.

EXPERIMENTAL

The retention data used were obtained isothermally at 150° using 12 ft. \times 1/4 in. O.D. aluminium columns with 10% stationary phase on 62-72 mesh acid washed and silanized Celatom, as previously reported³.

The intercepts of the retention plots of the homologous series were calculated from the line of best fit determined by regression analysis using a simple programmable calculator.

RESULTS AND DISCUSSION

The retention data of the esters examined are shown in Tables I and II as relative retentions (V_R) using *n*-nonane as standard and as retention indices (I). Figs. 1a and 1b show retention plots of the *n*-alkyl pivalates and the normal-acid-chain esters of the same carbon number, *i.e.* *n*-pentanoates, respectively, on a series of polysiloxane stationary phases of varying polar character. From Fig. 1a, it is evident that the retention of the branched esters is significantly reduced as compared with the normal esters (Fig. 1b). The behaviour on the non-polar phases follows a boiling-point relationship as the branching causes the usual reduction in boiling point relative to the straight-chain homologs. The retention of both series is increased as the polar nature of the phase is increased, although it is apparent that with the pivalates the increased retention over the range of phases is reduced. This effect, which might be expected as the polarizable groups of the esters are partially shielded from the interactive groups of the polar phases and the repulsive forces, and the solute retardation are not as great as with the straight-chain esters. The customary increased retention of methyl compounds occurs with both series of compounds.

The retention increments due to the carboxyl group of the *n*-alkyl esters on various phases have been reported previously³ and were found as the intercept of the linear retention relationship calculated from the line of best fit determined by regression analysis where the abscissa was considered as the total number of carbon atoms due to the alkyl groups. With the esters previously reported, the incremental value for the carboxyl group was observed to increase as the polar character of the stationary phase was increased, and the same effect is observed with the values determined for the pivalate series, which are shown in Table III together with values for the *n*-alkyl esters.

Figs. 2a and 2b show retention plots of the isoalkyl esters of pivalic and *n*-pentanoic acids, respectively, on the same phases. In common with the behaviour

TABLE II
RETENTION DATA FOR NORMAL AND ISOMERIC SATURATED ESTERS AND STANDARD SUBSTANCES ON ACCEPTOR
STATIONARY PHASES

Compound	Stationary phase													
	F-400		F-500		QF-1		XE-60		OV-225		SILAR 5CP		XF-1150	
	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I	V_R	I
Benzene	0.384	720	0.491	761	0.642	802	0.835	863	0.966	898	1.630	998	1.663	1014
Butanol	0.373	715	0.496	763	0.833	861	1.359	967	1.424	977	2.531	1090	3.101	1146
2-Pentanone	0.590	801	0.831	864	1.650	1017	1.427	977	1.483	986	2.519	1089	3.030	1139
Nitropropane	0.928	887	1.355	960	2.958	1151	3.345	1159	3.266	1150	6.630	1291	8.350	1379
Pyridine	0.893	880	1.244	943	2.175	1081	2.699	1113	3.178	1148	6.175	1275	6.100	1289
2-Methyl-2-pentanol	0.581	794	0.727	838	1.067	918	1.470	984	1.424	978	2.333	1073	2.675	1115
tert.-Butyl acetate	0.512	776	0.649	815	1.025	909	0.811	857	0.856	873	1.272	947	1.363	972
Methyl pentanoate	1.028	906	1.354	960	2.046	1067	1.803	1027	1.950	1042	3.075	1131	3.089	1145
Ethyl pentanoate	1.477	978	1.850	1021	2.836	1141	2.372	1085	2.647	1105	3.888	1180	3.822	1190
Propyl pentanoate	2.414	1074	3.004	1116	4.364	1240	3.675	1179	4.126	1196	6.025	1211	5.767	1277
Butyl pentanoate	3.944	1171	4.899	1212	6.582	1334	5.892	1279	6.496	1289	9.275	1361	8.533	1360
Pentyl pentanoate	6.435	1267	7.946	1307	10.009	1429	9.241	1375	10.185	1382	14.275	1451	12.756	1445
Hexyl pentanoate	10.449	1362	12.755	1400	15.118	1524	14.414	1470	16.143	1476	21.750	1539	19.022	1530
Isopropyl pentanoate	1.772	1014	2.211	1056	3.277	1174	2.601	1105	2.790	1116	3.900	1180	3.811	1190
Isobutyl pentanoate	3.242	1132	4.033	1174	5.714	1301	4.793	1235	5.118	1240	7.162	1307	6.878	1315
Isopentyl pentanoate	5.397	1233	6.704	1274	8.668	1397	7.606	1333	8.328	1340	11.450	1405	10.489	1404
Methyl pivalate	0.556	797	0.679	828	1.053	915	0.872	879	0.942	897	1.204	951	1.388	975
Ethyl pivalate	0.813	868	0.988	902	1.373	977	1.173	941	1.173	942	1.500	1000	1.615	1021
Propyl pivalate	1.337	962	1.617	1000	2.200	1087	1.850	1037	1.885	1038	2.315	1097	2.508	1128
Butyl pivalate	2.225	1059	2.741	1105	3.320	1183	2.872	1129	2.981	1131	3.685	1201	3.615	1217
Pentyl pivalate	3.636	1151	4.235	1191	5.107	1283	4.466	1222	4.673	1222	5.574	1294	5.400	1314
Hexyl pivalate	—	—	—	—	—	—	—	—	—	—	8.574	1391	8.138	1414
Isopropyl pivalate	0.941	896	1.136	930	1.640	1018	1.218	949	1.212	948	1.463	994	1.585	1016
Isobutyl pivalate	1.882	1027	2.222	1063	2.973	1157	2.421	1093	2.423	1090	2.833	1142	2.969	1169
Isopentyl pivalate	3.059	1119	3.605	1159	4.467	1252	3.699	1182	3.827	1181	4.537	1248	4.508	1270

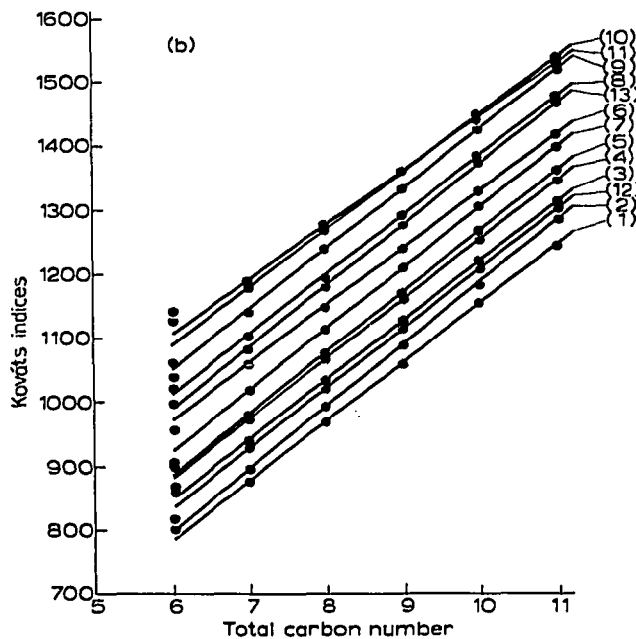
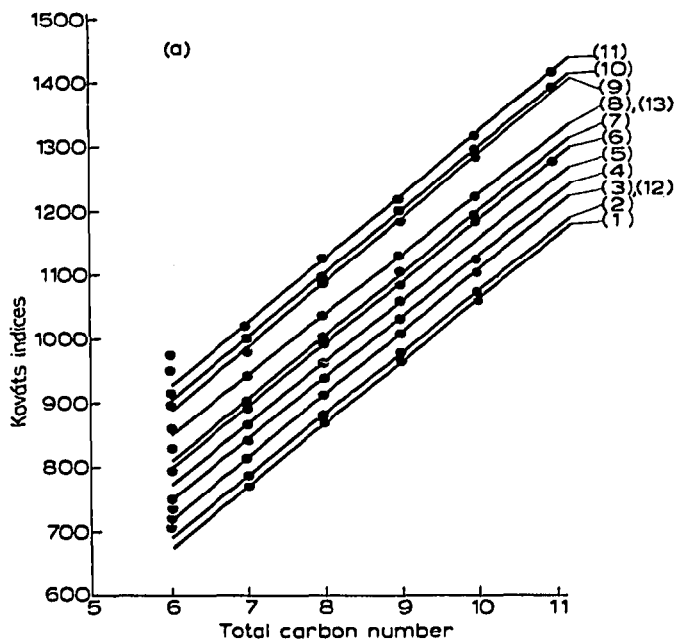


Fig. 1. Retention plots of (a) *n*-alkyl pivalates and (b) *n*-alkyl pentanoates on (1) SE-30, (2) DC-230, (3) OV-7, (4) DC-710, (5) F-400, (6) 100% Phenyl, (7) F-500, (8) OV-225, (9) QF-1, (10) SILAR 5CP, (11) XF-1150, (12) DC-530 and (13) XE-60.

TABLE III

RETENTION INCREMENT FOR CARBOXYL FUNCTION IN NORMAL STRAIGHT-CHAIN AND PIVALATE ESTERS

Stationary phase	Increment	
	Simple esters	Pivalate esters
SE-30	324	193
DC-230	320	218
OV-7	363	226
DC-710	417	281
100% Phenyl	548	314
F-400	417	301
F-500	473	321
XE-60	539	381
OV-225	558	384
QF-1	571	372
SILAR 5CP	663	413
XF-1150	718	441

shown in Figs. 1a and 1b, the retention of both series is also increased as the polar character of the phase is increased. However, the increased retention over the range of stationary phases is lower than with the isoalkyl pivalates.

The increased retention due to polar interactions, *i.e.* $I_{XF-1150} - I_{SE-30}$, being greatest with the *n*-alkyl esters, and decreasing with isoalkyl esters, *n*-alkyl pivalates and isoalkyl pivalates. Incremental values for the carboxyl group of the isoalkyl esters are not shown owing to the non-linear nature of some of the plots. Also with the esters reduced retention of the isopropyl compounds occurs, as discussed previously by Allen and Haken⁸, and sufficient data are not available to determine a reasonable line for comparison.

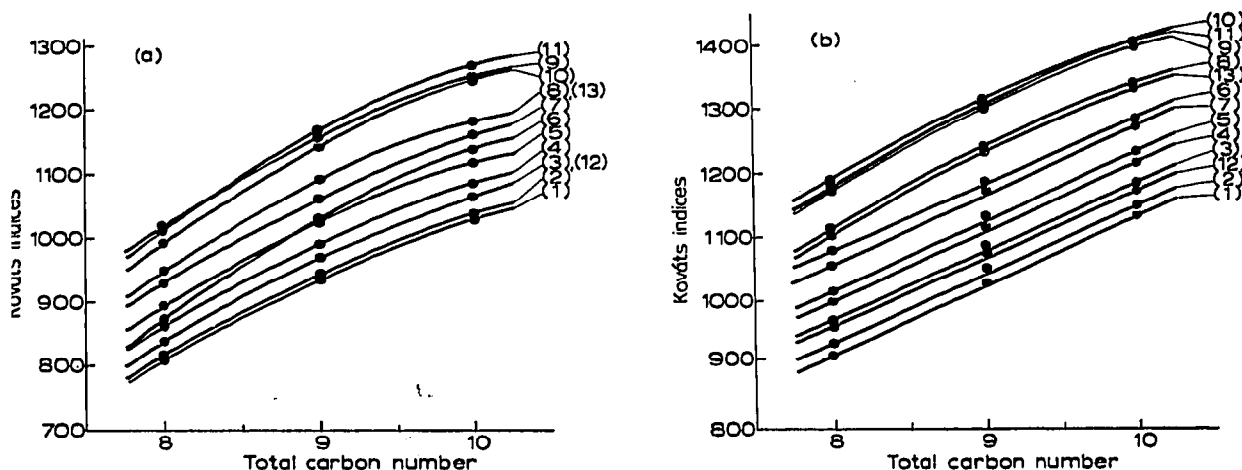


Fig. 2. Retention plots of (a) isoalkyl pivalates and (b) isoalkyl pentanoates on stationary phases as shown for Fig. 1.

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