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GAS-LIQUID CHROMATOGRAPHIC RETENTION BEHAVIOUR OF HINDERED ALIPHATIC ESTERS*

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SUMMARY

Relative retentions and Kováts retention indices of sixteen crowded aliphatic ethyl or methyl esters ($R_1R_2CHCO_2R$ or $R_1R_2R_3CCO_2R$; R = ethyl or methyl) have been systematically determined on nine stationary phases of increasing polar character from the non-polar branched-chain hydrocarbon $C_{87}H_{176}$ to the highly polar cyanopropylsiloxane Silar-10C. A qualitative pattern showing the retention behaviour of the branched acyl group of the esters is developed. An unexpectedly strong contribution of polar effect occurs with highly congested acyl groups in α,α,α -trialkyl esters.

INTRODUCTION

The pioneering work of James and Martin² in gas chromatography showed the effect of non-polar solvents and solutes on retention and, although the influence of the interaction of donor and acceptor groups in both species has been recognized, only qualitative applications have been possible. The elution of non-polar solutes on non-polar solvents according to boiling point or molecular weight has been extended to studies of simple esters which are of increased polar character³ where the elution order frequently follows the boiling points but is influenced by the shape of the molecule and the resulting steric hindrance. Where steric hindrance occurs, some screening of the interactive carbonyl group is possible and the increased retention expected with the use of more polar stationary phases is reduced.

Chain branching of the acyl group has been examined by considering the *n*-alkyl esters of pivalic and pentanoic acids on polysiloxane stationary phases of varying polar character⁴. The retention of both series increased with increasing polarity of the stationary phase, although with the pivalates the expected retention is reduced.

* Part XIV of the series "Gas chromatography of esters". For Part XIII, see ref. 1.

The effect is due to partial shielding of the polarizable groups of the esters from the interactive groups of the solvents. The retentions of the isoalkyl pivalates and *n*-pentanoates on the same stationary phases followed those of the normal esters, but the retentions of both series of esters were further reduced by the branched acid chain.

The retention of branched-chain esters has also been reported by Eidus *et al.*⁵, who published retention plots of α,α -dimethylalkanoic acids and their isobutyl esters on a polar column, *viz.*, 18% diethylene glycol succinate with 4% phosphoric acid. The retention order was α,α -dimethyl series < α -methyl series < α -ethyl series, and the first members of the dimethyl esters on both plots, *viz.*, pivalic acid and isobutyl pivalate, showed substantially reduced retentions compared with those of the other members of the series.

Recent developments in data processing with topological analysis⁶⁻⁸ allow a better understanding of the competition between polar and steric effects on the specific interactions between the solute and stationary phases. This information is necessary for physico-chemical developments such as simulation of adsorption and reactivity in catalysis⁸ or for analytical purposes where structural interpolation or extrapolation is used with structure-retention relationships in order to establish data banks⁹⁻¹². With this aim, systematic studies have been undertaken with hydrocarbon compounds and alkenes by gas-liquid chromatography^{6,7,11}, by gas-solid chromatography by emphasizing the effect of the support by the use of non-specific graphitized thermal carbon black¹³ and with specific adsorbents by using different cationic forms of ion exchangers^{8,14}.

In this study we investigated structural effects in highly congested alkylacyl groups, using a new series of hindered esters. Chain branching or lengthening makes different contributions to retention if it occurs in the acyl group or in the alkanol chain^{3,7}, and the effect in the vicinity of the carbonyl group was studied using a homologous set of hindered ethyl esters.

The paper considers the retention behaviour of a series of crowded esters, *viz.*, α,α -dialkyl- and α,α,α -trialkyl-substituted acid groups of ethyl esters, on a series of stationary phases of increasing polar character. A qualitative pattern showing the retention behaviour of the branched acyl group of the esters is developed. An unexpectedly strong contribution of the polar effect is present with highly congested alkyl groups in α,α,α -trialkyl-substituted esters.

EXPERIMENTAL

Synthesis

The structures of the esters are given in Table I. The procedures used for the preparation of the esters are summarized in Fig. 1 and outlined below.

α -Monosubstituted esters. Most of the compounds were commercially available, the others were prepared by esterification of the corresponding acids¹⁵.

α,α -Disubstituted acids. The α,α -disubstituted acids were prepared by Creger's method¹⁶. To a solution of 10.1 g (100 mmoles) of freshly distilled diisopropylamine (*i*-Pr₂NH) at 0°C, in 100 ml of tetrahydrofuran (THF), were added 100 mmoles (1 equiv.) of *n*-propyllithium (*n*-PrLi) in pentane. After stirring for 10 min, 45 mmoles of the acid in THF were added slowly and the mixture was stirred for 2 h. The alkyl iodide (1.10 equiv.) in THF containing hexamethylphosphoric triamide (HMPA)

TABLE I

STRUCTURES OF THE SERIES OF 19 HINDERED ESTERS, $R_1R_2R_3CCO_2R$

All are ethyl esters except No. 14, which is a methyl ester. Abbreviations: Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl.

| No. | Name | R_1 | R_2 | R_3 | R | Graph (acyl group) |
|-----|--|--------------|--------------|-------|-----|--------------------|
| 1 | Ethyl pentanoate | <i>n</i> -Pr | H | H | Et | |
| 2 | Ethyl 2,2-dimethylpropanoate | Me | Me | Me | Et | |
| 3 | Ethyl 2-methylbutanoate | Et | Me | H | Et | |
| 4 | Ethyl hexanoate | <i>n</i> -Bu | H | H | Et | |
| 5 | Ethyl 2,3-dimethylbutanoate | <i>i</i> -Pr | Me | H | Et | |
| 6 | Ethyl 3,3-dimethylbutanoate | <i>t</i> -Bu | H | H | Et | |
| 7 | Ethyl 2-ethyl-2-methylbutanoate | Et | Et | Me | Et | |
| 8 | Ethyl 2-ethyl-3-methylbutanoate | <i>i</i> -Pr | Et | H | Et | |
| 9 | Ethyl 2,2,3-trimethylbutanoate | <i>i</i> -Pr | Me | Me | Et | |
| 10 | Ethyl 2,3,3-trimethylbutanoate | <i>t</i> -Bu | Me | H | Et | |
| 11 | Ethyl 2,2-diethylbutanoate | Et | Et | Et | Et | |
| 12 | Ethyl 2-isopropyl-3-methylbutanoate | <i>i</i> -Pr | <i>i</i> -Pr | H | Et | |
| 13 | Ethyl 2-ethyl-3,3-dimethylbutanoate | <i>t</i> -Bu | Et | H | Et | |
| 14 | Methyl 2,2,3,3-tetramethylbutanoate | <i>t</i> -Bu | Me | Me | Me | |
| 15 | Ethyl 2-isopropyl-3,3-dimethylbutanoate | <i>t</i> -Bu | <i>i</i> -Pr | H | Et | |
| 16 | Ethyl 2-ethyl-2,3,3-trimethylbutanoate | <i>t</i> -Bu | Et | Me | Et | |
| 17 | Ethyl 3,3-dimethyl-2-tert.-butylbutanoate | <i>t</i> -Bu | <i>t</i> -Bu | H | Et | |
| 18 | Ethyl 3,3-dimethyl-2-isopropyl-2-methylbutanoate | <i>t</i> -Bu | <i>i</i> -Pr | Me | Et | |
| 19 | Ethyl 3,3-dimethyl-2,2-diethylbutanoate | <i>t</i> -Bu | Et | Et | Et | |

(0.20 equiv.) was added and stirring was continued overnight. The usual work-up was performed to give the α,α -disubstituted acids shown in Table II.

α,α -Disubstituted esters. The α,α -disubstituted acids were treated with an excess of freshly distilled thionyl chloride, refluxed for 1 h and poured into absolute ethanol. After stirring for 2 h, the usual work-up (pouring the mixture on to ice, alkalization, extraction) yielded the esters shown in Table III.

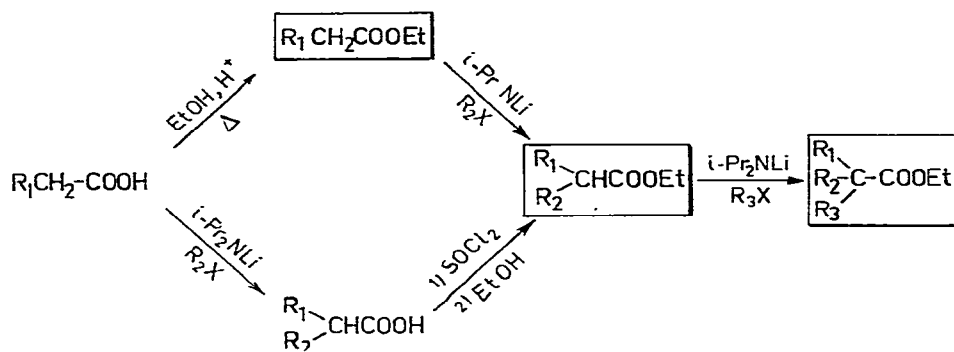


Fig. 1. General procedure for the preparation of the esters.

t-Bu-*i*-PrCHCOOEt has been described previously¹⁷ and *t*-Bu₂CHCOOEt by Newman *et al.*¹⁸ and Abruscato and Tidwell¹⁹.

α,α,α-Trisubstituted esters. To a solution of diisopropylamine (*i*-Pr₂NH) [3.15 equiv. in HMPA-THF (1:2) at 0°C] were added 3 equiv. of *n*-PrLi in pentane. After stirring for 10 min the *α,α*-disubstituted ester (1 equiv.) in HMPA-THF (1:2) was added slowly and the mixture was stirred for 2 h. Alkyl iodide (3 equiv.) in THF was then added with an exothermic reaction, during which the mixture was allowed to warm to ambient temperature. After stirring overnight, work-up was performed as usual²⁰.

The physical properties of the compounds are given in Tables II and III. All of the products were identified by their IR spectra (Perkin-Elmer 225), ¹H NMR spectra (Jeol C 60 HL) and mass spectra (Jeol D 100).

Chromatographic analysis

Chromatography was carried out using 12 ft. × 0.25 in. O.D. columns packed with 10% stationary phase on Chromosorb W AW DMCS, each operated isothermally at 120°C.

TABLE II

SYNTHESIS OF THE INTERMEDIATE *α,α*-DISUBSTITUTED ACIDS, R₁R₂CHCOOH. YIELDING AFTER TREATMENT WITH THIONYL CHLORIDE AND ETHANOL CORRESPONDING ESTERS

| R ₁ | R ₂ | Boiling point (°C) | |
|----------------|----------------|--------------------|---------------------------------|
| | | Experimental | Literature |
| <i>t</i> -Bu | <i>t</i> -Bu | 78–79* | 72–74 ¹⁸ |
| <i>t</i> -Bu | Et | 62–63 (25 mmHg) | 61–63 (25 mmHg) ¹⁹ |
| <i>t</i> -Bu | Me | 72–74 (18 mmHg) | — |
| <i>i</i> -Pr | <i>i</i> -Pr | 112–114 (15 mmHg) | 112–114 (15 mmHg) ²¹ |
| <i>i</i> -Pr | Et | 125–132 (15 mmHg) | — |
| <i>i</i> -Pr | Me | 99–102 (18 mmHg) | 105–107 (22 mmHg) ²² |

* Melting point.

TABLE III

SYNTHESIS OF α,α -DISUBSTITUTED ($R_1R_2CHCOOEt$) AND α,α,α -TRISUBSTITUTED ESTERS ($R_1R_2R_3CCOOEt$)

| R_1 | R_2 | R_3 | Boiling point ($^{\circ}C$) | |
|--------------|--------------|-------|-------------------------------|----------------------------------|
| | | | Experimental | Literature |
| Me | Me | H | 110-111 | 111 ²² |
| Et | Me | H | 132 | 131-133 (730 mmHg) ²² |
| <i>i</i> -Pr | Me | H | 51-52 (48 mmHg) | 51-53 (48 mmHg) ¹⁷ |
| <i>i</i> -Pr | Et | H | 48 (15 mmHg) | 53-55 (18 mmHg) ¹⁷ |
| <i>i</i> -Pr | <i>i</i> -Pr | H | 72-74 (18 mmHg) | 82-88 ²³ |
| <i>t</i> -Bu | Me | H | 61-63 (25 mmHg) | 61-63 (25 mmHg) ¹⁷ |
| <i>t</i> -Bu | Et | H | 67-72 (30 mmHg) | 82-88 ¹⁷ |
| <i>t</i> -Bu | <i>i</i> -Pr | H | 78-82 (15 mmHg) | — |
| <i>t</i> -Bu | <i>t</i> -Bu | H | 98-103 (15 mmHg) | — |
| <i>i</i> -Pr | Me | Me | 156-158 | — |
| <i>i</i> -Pr | <i>i</i> -Pr | Me | 100-102 (38 mmHg) | 100-102 (38 mmHg) ¹⁷ |
| <i>i</i> -Pr | <i>i</i> -Pr | Et | 84-86 (15 mmHg) | 83-87 (15 mmHg) ¹⁷ |
| <i>t</i> -Bu | <i>i</i> -Pr | Me | 96-98 (14 mmHg) | 91-92 (12 mmHg) ¹⁷ |
| <i>t</i> -Bu | Et | Et | 108-110 (15 mmHg) | 108-110 (15 mmHg) ²⁴ |
| <i>t</i> -Bu | <i>i</i> -Pr | Et | 99-102 (10 mmHg) | 98-103 (10 mmHg) ¹⁷ |

To increase the speed and accuracy of the determination of retention data, a Hewlett-Packard 5750 research gas chromatograph was interfaced with a 16K PDP 11/40 digital computer. The chromatograph employed a splitter and individually operated detectors, and retentions could be compared against values on a standard stationary phase. Injection was carried out with a Hewlett-Packard 7670A automatic sampler. Calculations of dead time and retention indices were conducted mathematically within the system, the injector being programmed to allow regular standardization with an alkane mixture.

RESULTS AND DISCUSSION

The influence of molecular weight, the effect of specific interactions between the hindered esters and the stationary phases of various polarities and the effect of branching in the acid chain, *i.e.*, in the acyl group, can be deduced from the data in Table IV and from Fig. 2. These acyl groups exhibit three different degrees of substitution (1, 2 and 3, respectively, in $R_1CH_2CO_2Et$, $R_1R_2CHCO_2Et$ and $R_1R_2R_3CCO_2Et$) with linear or branched-chain alkyl groups. The simplest ethyl esters, *i.e.*, the pentanoates (compounds 1, 2 and 3) have an acyl group with four carbon atoms. Their retentions, compared on the non-polar stationary phase SE-30, decrease with increasing degree of substitution of these acyl groups:

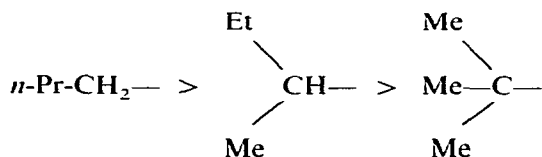











TABLE IV
 RETENTION DATA OF CROWDED ESTERS ON NINE STATIONARY PHASES OF INCREASING POLARITY AT 120°C
 RT = corrected retention time (sec); *I* = Kováts retention index; names of the compounds as in Table I.

| No. | Graph acyl group | C_8H_{17} | | SE-30 | | OV-7 | | OV-25 | | OV-105 | | PEG 400 | | Silar-7CP | | Silar-9CP | | Silar-10C | |
|-----|---------------------|-------------|----------|-------|----------|-------|----------|-------|----------|--------|----------|---------|----------|-----------|----------|-----------|----------|-----------|----------|
| | | RT | <i>I</i> | RT | <i>I</i> | RT | <i>I</i> | RT | <i>I</i> | RT | <i>I</i> | RT | <i>I</i> | RT | <i>I</i> | RT | <i>I</i> | RT | <i>I</i> |
| 1 | | | | 876 | | 941 | | 1014 | | | | | | | | | | | |
| 2 | | | | 771 | | 809 | | | | | | | | | | | | | |
| 3 | | 85.4 | 794 | 93.7 | 834 | 52.7 | 882 | 144.1 | 959 | 66.9 | 1151 | 104.0 | 1152 | 85.5 | 1185 | 91.5 | 1226 | 73.8 | 1263 |
| 4 | | | | 976 | | 1045 | | 1118 | | | | | | | | | | | |
| 5 | | 136.1 | 878 | 134.9 | 908 | 77.2 | 957 | 202.6 | 1030 | 90.2 | 1233 | 138.0 | 1220 | 114.5 | 1260 | 116.2 | 1296 | 89.8 | 1334 |
| 6 | | 120.1 | 856 | 116.2 | 878 | 65.7 | 925 | 967.6 | 991 | 76.7 | 1188 | 118.5 | 1183 | 97.7 | 1219 | 104.2 | 1264 | 86.4 | 1320 |
| 7 | | 217.1 | 960 | | | 111.2 | 1028 | 281.6 | 1099 | 112.2 | 1292 | 170.4 | 1276 | 141.2 | 1319 | 155.5 | 1381 | 113.4 | 1418 |
| 8 | | 212.4 | 957 | 194.7 | 983 | 112.0 | 1030 | 283.6 | 1101 | 114.2 | 1287 | 174.2 | 1281 | 143.0 | 1317 | 150.6 | 1383 | 114.1 | 1420 |
| 9 | | 201.6 | 947 | 186.4 | 971 | 105.2 | 1017 | 265.6 | 1087 | 107.7 | 1281 | 162.9 | 1265 | 136.2 | 1304 | 144.7 | 1360 | 107.9 | 1400 |
| 10 | | 187.9 | 935 | 178.7 | 965 | 101.7 | 1011 | 257.8 | 1081 | 106.7 | 1276 | 160.7 | 1262 | 134.2 | 1301 | 146.2 | 1363 | 109.1 | 1404 |

| | | | | | | | | | | | | | | | | | | | |
|----|---|-------|-------|-------|------|-------|------|--------|------|-------|------|-------|------|-------|-------|-------|-------|-------|------|
| 11 |  | 372.9 | 1056 | 319.2 | 1083 | 187.2 | 1131 | 446.6 | 1204 | 171.7 | 1048 | 265.7 | 1383 | 218.0 | 1425 | 226.7 | 1484 | 125.1 | 1524 |
| 12 |  | 296.9 | 1016 | 266.9 | 1047 | 153.2 | 1091 | 375.1 | 1159 | 141.7 | 1356 | 216.9 | 1334 | 179.2 | 1375 | 172.2 | 1408 | 124.9 | 1443 |
| 13 |  | | 248.7 | 1033 | | 137.7 | 1070 | 345.1 | 1142 | | | | | | 161.0 | 1359 | 117.6 | 1425 | |
| 14 |  | 218.4 | 961 | 198.4 | 987 | 115.7 | 1036 | 307.1 | 1117 | 128.7 | 1330 | 204.2 | 1320 | 167.5 | 1358 | 171.7 | 1407 | 128.9 | 1452 |
| 15 |  | 408.1 | 1072 | 349.4 | 1102 | 200.0 | | 672.8 | | 160.2 | 1389 | 254.4 | 1372 | 208.0 | 1413 | 201.2 | 1457 | 219.6 | 1509 |
| 16 |  | 546.4 | 1124 | 432.9 | 1146 | 253.2 | 1194 | 641.6 | 1271 | 221.2 | 1477 | 348.4 | 1448 | 286.0 | 1495 | 280.5 | 1543 | 201.1 | 1606 |
| 17 |  | 688.4 | 1165 | 525.9 | 1185 | 311.0 | 1228 | 737.9 | 1298 | 232.7 | 1491 | 375.9 | 1466 | 295.2 | 1504 | 288.2 | 1550 | 205.6 | 1587 |
| 18 |  | 966.7 | 1222 | 679.7 | 1237 | 419.0 | 1286 | 1046.1 | 1371 | | | 556.2 | 1560 | | | 445.5 | 1670 | 317.4 | 1713 |
| 19 |  | 966.9 | 1234 | 716.7 | 1248 | 445.5 | 1297 | 1080.6 | 1377 | 342.7 | 1597 | 566.4 | 1564 | 436.7 | 1604 | 428.5 | 1659 | 301.1 | 1698 |

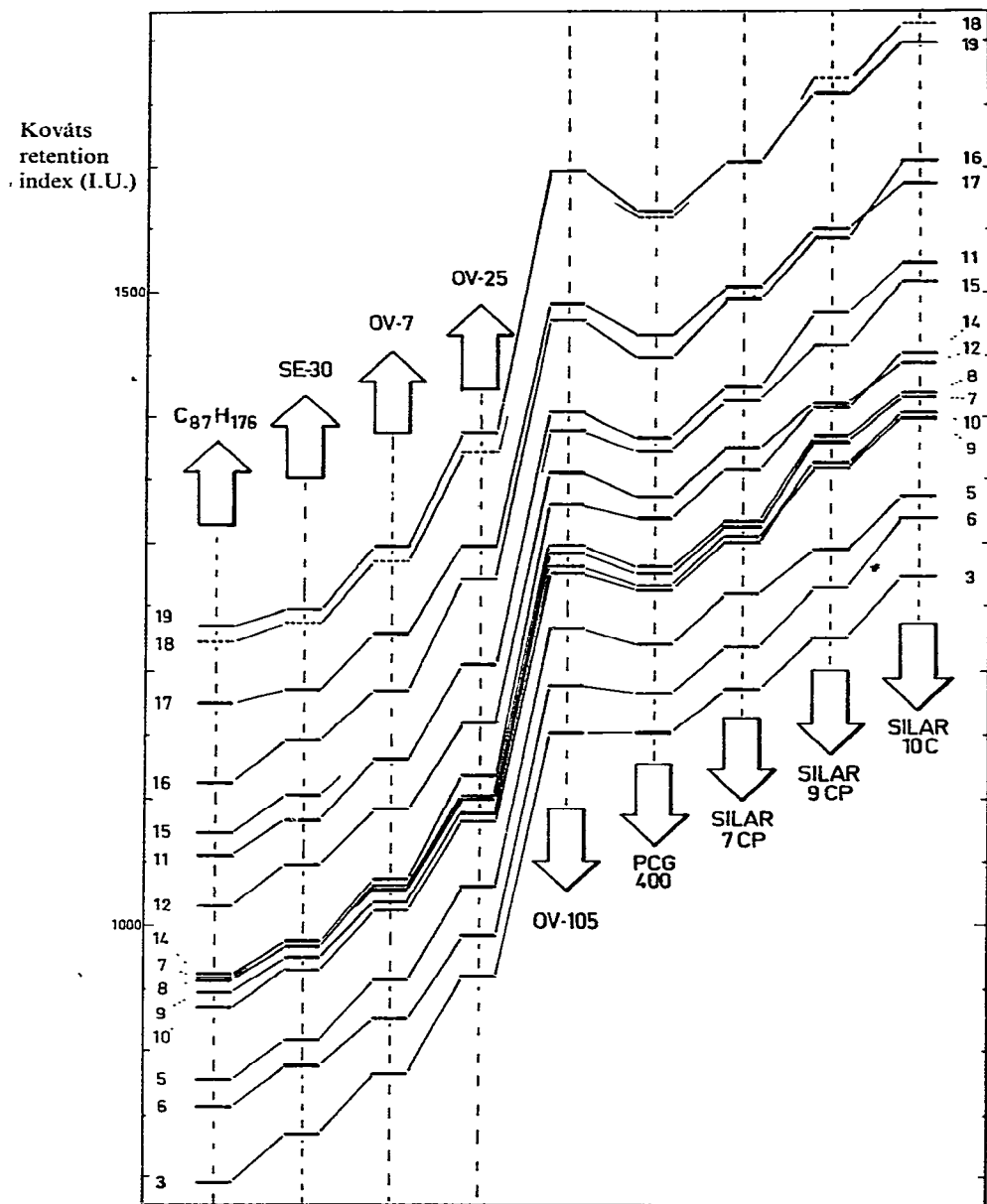
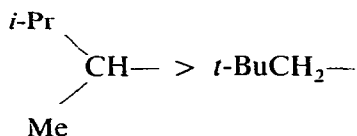


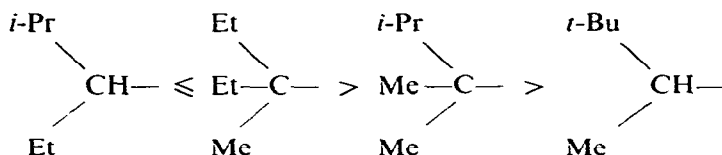
Fig. 2. Retention indices (I.U.) of hindered esters (ordinate) for nine stationary phases of increasing polarity. The variation in selectivity of these esters and even of the retention order for some of them with the more polar Silar phases can be observed.

The hexanoate esters have an acyl group with five carbon atoms, and allow comparison of the ester with a neopentyl group with one containing an isopropyl and a methyl group, which has a higher retention on all of the stationary phases studied:



The retention increases by about 450 index units (I.U.) from the non-polar $\text{C}_{87}\text{H}_{176}$ up to the highly polar Silar-10C, and the relative retentions, estimated from the range of the Kováts retention index, δI , decreases from 30 I.U. on SE-30 to 14 I.U. on Silar-10C, *i.e.*, by a factor of about 2 (Fig. 3).

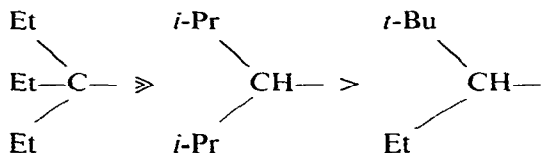
The retention order of heptanoate esters, which have six carbon atoms in the acyl group (compounds 7, 8, 9 and 10), is as follows on most stationary phases:



The first two groups, $i\text{-PrEtCH—}$ and $\text{Et}_2\text{MeC—}$, exhibit very similar retentions, the maximal range of δI being only 5 I.U. A slight inversion of retention seems to take place with the non-polar $\text{C}_{87}\text{H}_{176}$, but it is at the limit of the experimental precision. The range of Kováts retention indices for the above set of four compounds is 25 I.U. on $\text{C}_{87}\text{H}_{176}$ and only 20 I.U. on Silar-10C, despite an increase in retention of about 500 I.U. with this very polar stationary phase (Fig. 3).

Comparison of the retentions of the ethyl ester $t\text{-BuMeCHCO}_2\text{Et}$ (compound 10) and the methyl ester $t\text{-BuMe}_2\text{CCO}_2\text{Me}$ (compound 14) with the same total carbon number shows the relative influence of substitution by a methyl group in the α -position of the acyl group instead of substitution by a methyl group in the α -position of the alkanol group. Replacement of a hydrogen atom by a methyl group in the α -position of the acyl group increases the retention by 25 I.U. on the non-polar $\text{C}_{87}\text{H}_{176}$ and by 48 I.U. on Silar-10C. For less crowded esters, substitution by a methyl group in the α -position of the acyl group contributes less to the retention (about 56 I.U. on the polar Silar-5CP), as has been shown on a statistical basis by topological analysis⁷.

The octanoate esters (compounds 11, 12 and 13) have an acyl group with seven carbon atoms. The α,α,α -trisubstituted $\text{Et}_3\text{CCO}_2\text{Et}$ ester shows the greatest retention:



The range of Kováts retention indices on the non-polar SE-30 is large, $\delta I = 50$ I.U.

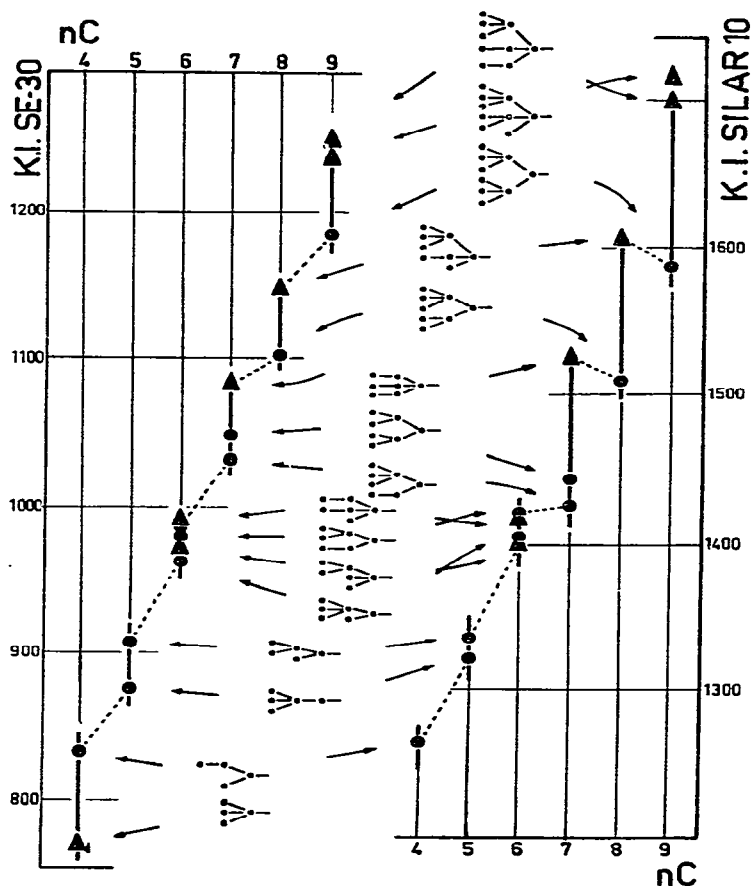


Fig. 3. Retentions of hindered esters expressed as Kováts retention indices (K.I.) at 120°C on non-polar SE-30 stationary phase and on highly polar Silar-10C stationary phase versus the carbon number (nC) of the acyl groups. For $nC \geq 7$ the highly congested α, α, α -trisubstituted esters exhibit unexpectedly the highest retention and the greatest sensitivity to the polarity of the stationary phase. ●, α, α -Disubstituted esters; ▲, α, α, α -trisubstituted esters.

compared with 25 I.U. on $C_{87}H_{176}$ and about 18 I.U. on SE-30 for the above set of four heptanoate esters. However, there is a considerable increase in the range δI when the polarity of the stationary phase increases; $\delta I = 101$ I.U. on the very polar Silar-

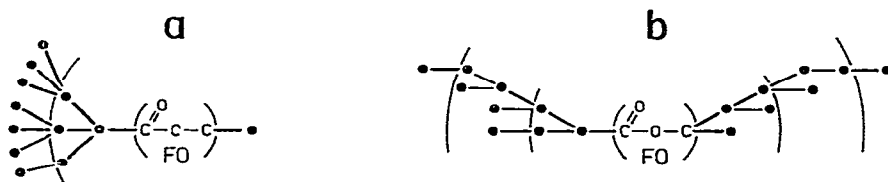
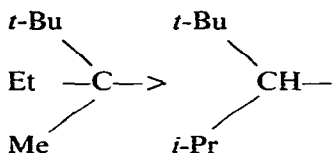


Fig. 4. (a) Superposition of elementary ester chemical graphs gives a trace characteristic of the studied population of 16 crowded esters. (b) Trace of a population of 99 esters with low or medium steric strains and which has been the subject of a previous physico-chemical study⁷. [The pattern (COOC) is taken as the focus FO].

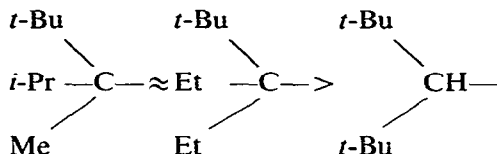
10C, and this increase in δI by a factor of 2 increases greatly the difference in retention between the α,α,α -trisubstituted and the α,α -disubstituted esters.

The two nonanoate esters (compounds 15 and 16) have eight carbon atoms in the acyl group. One is α,α,α -trisubstituted and the other is α,α -disubstituted. A marked difference in retention is observed on $C_{87}H_{176}$, where $\delta I = 52$ I.U., and again this selectivity increases almost by a factor of 2 on the more polar Silar-10C, where $\delta I = 97$ I.U.



In a C_6 acyl group the contribution of the (Et, Me) and i -Pr groups is scarcely differentiated and in the presence of a t -Bu group an (Et, Me) group exhibits a stronger retention than the i -Pr group.

The effect of the degree of substitution (α,α - and α,α,α -) is also apparent with the decanoate ethyl esters (compounds 17, 18 and 19). The order of retention for the nine carbon atom acyl groups is as follows on the more polar stationary phases:



but an inversion of the retention order is observed for the first two esters, of the α,α,α -substituted type, when the polarity of the stationary phase decreases from the medium polar PEG 400 to the non-polar $C_{87}H_{176}$.

For this set of compounds the range of δI is large even with the non-polar $C_{87}H_{176}$, where $\delta I = 69$ I.U., and δI increases greatly with increasing polarity of the stationary phase, to 126 I.U. on Silar-10C. The difference in retention between the α,α - and α,α,α -esters increases from 55 I.U. to 111 I.U. on the same stationary phases.

CONCLUSION

If the structure $\begin{array}{c} \text{O} \\ || \\ \text{C}-\text{O}-\text{C} \end{array} \text{F}$ is used as a basis, *i.e.*, as the focus FO, the crowded esters which have been systematically studied here have chemical graphs which are included in the trace shown in Fig. 4a, as defined by topological analysis^{6,7}. Comparison with Fig. 4b, for a series of 99 aliphatic esters^{25,26} studied previously by topological analysis⁷, indicates possible strains in the acyl groups of this series of hindered esters.

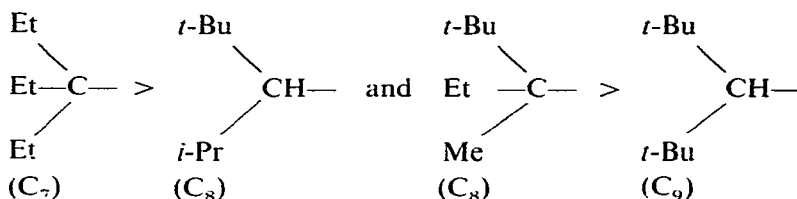
This study offers a coherent series of compounds for investigating contributions of steric effects to possible screening of the interactive carbonyl group and for studying how the increased retention expected with the use of more polar stationary phases is relatively reduced.

As the acyl groups of the set of esters studied are limited to the first environment defined by two layers of concentric carbon atoms, then as the carbon number of the acyl group is increased the overall steric effects of the constitutive substituents are increased from C_4 to C_9 .

The following trends are observed:

(a) On non-polar stationary phases the crowded ethyl esters are eluted according to their molecular weight, *i.e.*, according to the carbon atom number of the acyl group. The lower members with acyl groups (C_4 – C_6) have a medium steric effect as evaluated with the revised Taft steric constants $-E'_S$ ($1 < -E'_S < 3.54$)²⁷. The contribution of steric groups to lowering the retention is predominant and the degree of substitution of the α -carbon of the acyl group has a minor influence.

(b) When the polarity of the stationary phase is greatly increased, the higher members with acyl groups (C_7 – C_9) have a strong steric effect ($5.01 < E'_S < 7.56$). The difference in retention between the α,α,α -trisubstituted esters and their isomeric α,α -disubstituted isomers is increased by a factor of 2. The considerable increase in retention for the trisubstituted α,α,α -esters with an acyl group containing seven or more carbon atoms must be emphasized. Fig. 1 shows that on the polar Silar stationary phases the compounds are not eluted according to their molecular weight. A trisubstituted α,α,α -octanoate is eluted after a disubstituted α,α -nonanoate or a trisubstituted α,α,α -nonanoate, which is eluted after a α,α -disubstituted decanoate.



Therefore, when a highly congested alkyl group is present, even if some screening of the interactive carbonyl is possible, the increased relative retention expected with the use of more polar stationary phases is not reduced but increased. This is opposite to what would have been expected by extrapolation of the behaviour of esters with an alkyl group with a medium steric effect⁷. This suggests that the polarity of the carbonyl group is increased with such congested alkyl groups, causing stronger specific interactions.

Although the data presented here provide qualitative indications of the influence of branching on retention in the acyl group of aliphatic esters, a quantitative analysis of these effects and of the specific interactions needs to be established with a DARC topological analysis⁶⁻⁸. Further, a complementary quantitative study is currently underway to determine precisely the competition between polar and steric effects based on information deduced from IR spectroscopic data and relative to the corresponding hindered acids, in order to explain the unexpected sensitivity to polarity of the stationary phase in the case of highly congested alkyl groups.

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