## Notes

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### Effect of terminal "groups" on gas–liquid chromatographic retention times of long-chain compounds: A case of tail *versus* dog

Among the modified long-chain fatty acids for which GLC retention data have been tabulated for a full range of isomers are *cis* and *trans* octadecenoates[1], methylene-interrupted *cis,cis*-octadecadienoates[2], monomethyl-branched octadecanoates[3], nonynoates[4] and dodecynoates[1], and methyleneoctadecanoates (cyclopropanoids)[5]. Except for the latter class the general rule is that the ultimate or terminal isomer will have a retention time less than that of the penultimate isomer and often similar to that of the next isomer adjacent to the penultimate isomer.

The latter type of behaviour is known to be associated with boiling points. For example, in the *n*-octenes the elution order of isomers is 1, 3, 2 on both a polyester and squalane, corresponding to boiling points of 121.8°, 122.7° and 125.0° (ref. 6). Vapour pressures in isomeric structures are broadly considered to be maximal with the most highly centralised structure. Generally boiling points for higher molecular weight compounds are unknown, but a relationship between boiling point and GLC retention time has been explored definitively for isomeric alkylbenzenes[7]. As part of this study retention times were determined on Apiezon L at 210° and 240°. Thus ratios $t_{210°} \div t_{240°}$ for phenyldodecane isomers eluting in isomer order 6, 5, 4, 3, 2, 1 are 1.91, 1.91, 1.91, 1.93, 1.97 and 2.08. Evidently when a structure is asymmetric, vapour pressure is sensitive to temperature modification.

These observations came to mind in considering the anomalous behaviour of the cyclopropanoids and it was noted that methyl cyclohexylundecanoate[8] seemed peculiarly sensitive to GLC operating temperatures for a nominally fully saturated system (compare insensitivity of apolar methyl-branched acids[3]). On a modified EGA substrate ECL values were: 19.12 at 207° and 18.84 at 178°. On Apiezon L they were 18.00 at 207° and 17.82 at 180°. Other values (Table I) were determined in our laboratory. Presumably this sensitivity would be due to the asymmetry generated by a $C_6$ ring (terminal group) attached to a $C_{11}$ chain (base chain).

When a variety of structures commonly regarded as terminal $C_x$ "isomers" were re-examined from this novel view point of a $C_{x-n}$ base chain plus a $C_n$ terminal group (Table I) it was noted that the differences ($\Delta$) between the experimental ECL value and the total carbons in the terminal group plus the base chain, for Apiezon L, could be graded in approximate proportion to the base chain carbons divided by the terminal group carbons. The $C_{15}$ $\omega$-alicyclics fit particularly well into the series, and represent data from one laboratory. On polyester liquid phases this group of structures is also an adequate and coherent demonstration of $\Delta$ gradient but the bulk of the polyester data are modified somewhat by the polarity of the different functional groups as well as differences among the polyesters employed.

It seems probable that the positive $\Delta$ value of +0.38 as an indication of molecular asymmetry is adequate to explain the anomalous behaviour of 17,18-methyleneoctadecanoate relative to the balance of the octadecanoate-based series of cyclo-

ABLE I

SSIBLE PHYSICAL BASIS FOR MODIFICATION OF RETENTION TIME BY RELATING TOTAL CARBONS IN A BASE CHAIN THE TOTAL CARBONS IN A TERMINAL GROUP WHICH IS ATTACHED TO IT

| *ter* | *Base chain* | *Terminal group* | *Apiezon L* | | *Polar* | | *Polyester*[a] |
|---|---|---|---|---|---|---|---|
| | | | *ECL* | *Δ* | *ECL* | *Δ* | |
| -Cyclohexylundecanoate[4] | $C_{11}$ | $C_6$ | 17.92 | +0 92 | 18.40 | +1.40 | BDS |
| -Cyclohexylnonanoate[11] | $C_9$ | $C_6$ | 15.9 | +0 9 | 16 7 | +1 7 | Reoplex |
| -Cyclopentyldecanoate[11] | $C_{10}$ | $C_5$ | 15.8 | +0 8 | 16 5 | +1 5 | Reoplex |
| Cyclobutylundecanoate[11] | $C_{11}$ | $C_4$ | 15.6 | +0 6 | 16 1 | +1 1 | Reoplex |
| aulmoograte[12] | $C_{13}$ | $C_5$[b] | 18 90 | +0 90 | 20.50 | +2.50 | PEGS |
| ydnocarpate[12] | $C_{11}$ | $C_5$[b] | 16 85 | +0 85 | 18.65 | +2.65 | PEGS |
| ,18-Methyleneoctadecanoate[5] | $C_{16}$ | $C_3$ | 19 38 | +0 38 | 20 04 | +1.04 | NPGS |
| -Dodecynoate[1] | $C_{10}$ | $C_2$ | 12 01 | +0 01 | 14 00 | +2 00 | NPGS |
| ,18-Octadecenoate[1] | $C_{16}$ | $C_2$ | 17 89 | −0 11 | 18 49 | +0 49 | NPGS |
| ,17-Octadecadienoate[2] | $C_{15}$ | $C_5$ | 17.80 | −0 20 | 19 04 | +1 04 | NPGS |
| -Methyloctadecanoate[3] | $C_{16}$ | $C_3$ | 18 56 | −0 44 | 18 60 | −0 40 | BDS |

[a] The lowest polarity polyester is selected if there are data for more than one
[b] Cyclopentenyl ring.

propanoid isomers. The negative value (−0.44) for 17-methyloctadecanoate, which has a terminal group analogous to the cyclopropanoid ring but of an apolar non-rigid structure, exemplifies the more familiar types of isomeric series where boiling points are not exaggerated by molecular asymmetry.

STROCCHI *et al.*[9] have considered the relationship between molecular configuration in linear chains and GLC retention times. They mention that methyl 9-(2-*n*-propylcyclohexa-3,5-diene)nonanoate ($C_{18}$) has a centralised structure which should reduce retention time relative to $C_{18}$ straight-chain compounds, yet has an enhanced Apiezon L ECL value of 18.14. The *Δ* value of +0.14 does not match anticipated levels for a base chain of 9 and a terminal group of 9 (compare cyclohexylundecanoate and nonanoate) and therefore as far as GLC is concerned this structure is essentially a $C_{14}$ chain bridged across carbons 10 and 11 and there is no strong terminal effect. STROCCHI *et al.* are therefore probably correct in considering the conjugated diene as a major factor in increasing retention time, slightly offset by the centralised structure relative to linear $C_{18}$ fatty acids with conjugated dienes.

As a general concept asymmetry due to terminal groups can of course also predict elution order of non-fatty acid compounds. For example 1-cyclohexylnonadecane, 1-cyclopentyleicosane (both $C_{25}H_{50}$) and 2,2-dimethyltricosane ($C_{25}H_{52}$) have respective retention times (mm) on Apiezon L of 80.5, 75.5 and 41.2 (ref. 10). The base chain and terminal group ratios rank in corresponding order of 19:6, 20:5 and 21:4.

Since synthesis of new long-chain compounds is often most facile through attachment of a large group to the *ω*-position of a base chain, a knowledge of whether *Δ* were positive or negative could indicate the relative GLC behaviour of adjacent isomers which might be more difficult to synthesise.

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