

CHROM. 15,275

Note

Gas chromatography of homologous esters

XVIII*. Polychlorinated propionate and butyrate esters

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(Received August 12th, 1982)

A recent paper¹ has considered the retention behaviour of the methyl and chloromethyl esters of isomeric monochloro esters of C₂-C₁₈ *n*-carboxylic acids²⁻⁴ and of the corresponding monochloro esters of the isomeric C₅ aliphatic acids⁵.

The effect on retention of the position of the chlorine substituent and of branching in the acid chain shown in these reports was compared with the results from other studies on aliphatic esters containing a second and variable structural parameters.

The present work extends the earlier study using recently available data^{6,7} on the mono- and dichloro esters of *n*-butyric acid and on all the chlorinated esters of propionic acid^{8,9} such that the effect on retention of chlorine substituents in all of the positions in the chain is apparent.

EXPERIMENTAL

A Varian Model 2400 gas chromatograph with flame ionisation detector was used for the analyses. Glass capillary columns coated with 3% Carbowax 20M were used with temperature programming from 50°C at 6°C/min. The retention data were recorded as uncorrected retention times.

RESULTS AND DISCUSSION

The retention data for the methyl esters of mono- and dichlorobutyric acids are shown in Table I while the retention behaviour relative to the position of substitution is shown in Fig. 1.

The monochloro esters follow the trend previously observed for longer chain esters, where the retention increased with the distance of the chlorine atom from the carbonyl group, the ω - or terminally substituted compound having the highest retention due to minimisation of acceptor-donor effects.

Of the dichloro esters the 2,2-homologue has, predictably, the lowest retention time while the 3,3- and 4,4-homologues show progressively higher retention times, the

* Part XVII: G. Crank and J. K. Haken. *J. Chromatogr.*, 245 (1982) 346-349.

TABLE I
RETENTION TIMES OF MONO- AND DICHLOROBUTYRATE ESTERS

<i>Compound</i>	<i>Retention time (sec)</i>
Methyl butyrate	141
Methyl 2-chlorobutyrate	223
Methyl 3-chlorobutyrate	248
Methyl 2,2-dichlorobutyrate	282
Methyl 4-chlorobutyrate	340
Methyl 3,3-dichlorobutyrate	340
Methyl <i>erythro</i> -2,3-dichlorobutyrate	374
Methyl <i>threo</i> -2,3-dichlorobutyrate	484
Methyl 4,4-dichlorobutyrate	513
Methyl 2,4-dichlorobutyrate	561
Methyl 3,4-dichlorobutyrate	595

compounds following the pattern of the 2-, 3- and 4-chloro esters. The retention time of the 2,3-dichloro isomer is higher than that of the 3,3-isomer. that of the 2,4-isomer is similarly higher and the 3,4-dichloro ester shows the highest retention time. The polar effect of two chlorine substituents is maximised when the two atoms are not attached to the same carbon atom, which is simply due to the bulkiness of the substituents.

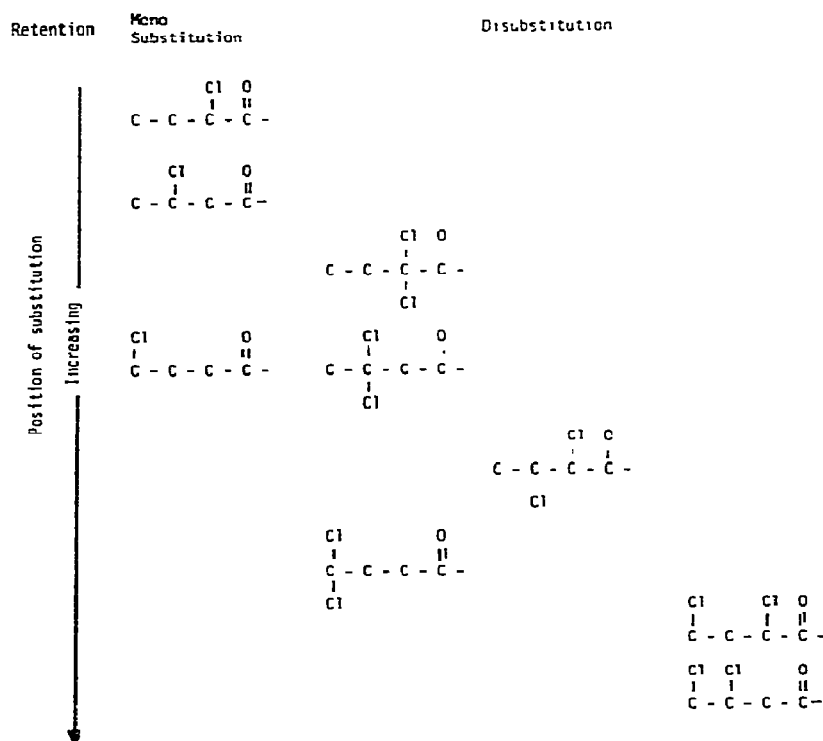


Fig. 1. Structure and retention behaviour of mono- and dichlorobutyrate esters.

The effect of further substitution may be observed from the data of the eleven methyl chloropropionates (Table II) while the retention behaviour relative to the position of the substituents is shown in Fig. 2. The increase in retention in the mono- and dichloropropionates followed the same pattern as for the corresponding butyrate esters.

As expected, the trichloropropionates have increased retention times and the 3,3,3-trichloro ester, due to attachment of three substituent groups, exhibits a lower retention than the 2,2,3-trichloro ester which, in turn, has a lower retention than the 2,3,3-isomer with terminal di-substitution.

The same pattern is observed for the two tetra-substituted isomers, where terminal di-substitution produces greater retention than terminal tri-substitution. The pentachloropropionate, with an additional chlorine substituent, shows the greatest retention of the series.

The two ester series generally follow the same retention pattern with substitution, and it is possible, by observing the following simple rules, to predict the elution behaviour of longer chain polychlorinated esters.

(1) The retention of an ester with single chlorine substitution increases as the distance from the carbonyl increases and retention is maximised with substitution in the terminal (ω) position.

(2) ω, ω di-substitution produces lower retention than $\omega, \omega - 2$ and $\omega, \omega - 1$ di-substitution.

(3) With trichloro esters retention is maximised with ω -di-substitution. The retention data, if available as retention indices, would allow the relative contributions of each substituent to be shown as retention increments as have been used with many series of saturated and unsaturated aliphatic esters.

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