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Note

Gas chromatography of homologous esters

XXIV*. Studies of chlorinated methyl propanoates and butanoates on a non-polar capillary column

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This work extends our earlier capillary gas chromatographic study of the chlorinated methyl propanoates[1,2] and of methyl mono- and dichlorobutanoates[2], which were examined using polar Carbowax 20M and non-polar SE-30 stationary phases with temperature programming, and of subsequent work[3] in which the effect on retention of chlorine substituents in all positions of the chain was considered on the Carbowax 20M stationary phase.

This work shows the retention indices and the effect of increments of the same series of esters on a dimethylpolysiloxane (OV-101) capillary column at increasing temperatures from 80 to 120°C.

EXPERIMENTAL

The esters (either prepared in the laboratory or of authentic commercial origin) were chromatographed on a Perkin-Elmer Sigma 3 instrument with a vitreous silica OV-101 wall-coated open tubular column (25 m × 0.30 mm I.D.), supplied by SGE (North Melbourne, Australia). Nitrogen was used as the carrier gas at a flow-rate of 1 ml/min with a splitting ratio of 1:20. The column temperatures used were 80, 100 and 120°C with the injector and flame-ionization detector operated at 275°C. Retention times were measured from the time of sample injection and the retention indices were determined off-line using a Vector M2 microprocessor system, the dead volume being first determined by regression analysis from a series of *n*-alkanes using the procedure of Grobler and Balizs[4].

RESULTS AND DISCUSSION

The retention indices of the methyl esters of the chloropropanoic acids are

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TABLE I

RETENTION INDICES OF METHYL CHLOROPROPANOATES ON OV-101 AT 80–120°C

Methyl ester	*80°C*	*100°C*	*120°C*
Propanoic acid	618	627	629
2-Chloropropanoic acid	768	780	781
3-Chloropropanoic acid	824	831	833
2,2-Dichloropropanoic acid	848	854	859
3,3-Dichloropropanoic acid	914	914	914
2,3-Dichloropropanoic acid	925	927	927
3,3,3-Trichloropropanoic acid	1017	1018	1015
2,3,3-Trichloropropanoic acid	1027	1029	1031
2,2,3-Trichloropropanoic acid	1028	1030	1031
2,3,3,3-Tetrachloropropanoic acid	1131	1137	1137
2,2,3,3-Tetrachloropropanoic acid	1149	1157	1156
Pentachloropropanoic acid	1260	1271	1275

shown in Table I, and those of the methyl esters of the mono- and dichlorobutanoic acids in Table II.

The increased retention of the monochloro esters with increasing distance between the chlorine atom and the carbonyl group is as previously reported for longer chain monochloro esters[5]. Little real difference occurs with the 2- and 3-monochloro esters, although substantial enhancement occurs in common with other series[3] with the terminal or ω position, as shown in Table III. Methyl dichloropropanoates partly follow the expected pattern, the 2,2-diester having a lower retention than the terminal 3,3-diester; the 2,3-diester, however, shows a slightly greater retention.

The methyl dichlorobutanoates follow the elution pattern previously reported[2], the separations being little influenced by isothermal or temperature programmed operation. The 2,2- and 3,3-diesters show similar retentions, although the 3,3-diester has a slightly greater retention at the lowest temperature. The 4,4-diester has a higher retention than the 3,3-diester and marginally lower than the 3,4- and 2,4-diesters.

TABLE II

RETENTION INDICES OF METHYL CHLOROBUTANOATES ON OV-101 AT 80–120°C

Methyl ester	*80°C*	*100°C*	*120°C*
Butanoic acid	717	710	709
2-Chlorobutanoic acid	863	861	859
3-Chlorobutanoic acid	869	864	859
4-Chlorobutanoic acid	937	933	927
2,2-Dichlorobutanoic acid	958	957	949
3,3-Dichlorobutanoic acid	960	958	949
erythro-2,3-Dichlorobutanoic acid	978	978	971
threo-2,3-Dichlorobutanoic acid	1011	1009	1001
4,4-Dichlorobutanoic acid	1047	1045	1037
3,4-Dichlorobutanoic acid	1054	1055	1046
2,4-Dichlorobutanoic acid	1057	1056	1047

TABLE III

RETENTION INCREMENTS OF CHLORINE SUBSTITUENTS IN METHYL CHLOROPROPANOATES AT 80°C

Methyl ester	*ΣΔCl*	*Σ1Cl*	*Σ2Cl*	*Σ3Cl*	*Σ4Cl*	*Σ5Cl*	*ΔCl*
Propanoic acid							
2-Chloropropanoic acid	150	150					150
3-Chloropropanoic acid	206	206					206
2,2-Dichloropropanoic acid	230		230				115
3,3-Dichloropropanoic acid	296		296				148
2,3-Dichloropropanoic acid	307		307				154
3,3,3-Trichloropropanoic acid	399			399			133
2,3,3-Trichloropropanoic acid	409			409			136
2,2,3-Trichloropropanoic acid	410			410			137
2,3,3,3-Tetrachloropropanoic acid	513				513		128
2,2,3,3-Tetrachloropropanoic acid	531				531		133
Pentachloropropanoic acid	642					642	128

The polar effect of the two chlorine substituents is maximized when the two bulky substituents are not attached to the same carbon atom. A greater difference in retention of these three esters is not as observed on the Carbowax 20M phase owing to the absence of the added polar forces.

The effects of the higher degrees of chlorination are largely as previously observed on Carbowax 20M[3,6].

A study of the incremental retention index values of chlorine substituents is shown for the chloropropanoate and chlorobutanoate esters in Tables III and IV, respectively. Table III shows that with the methyl chloropropanoates the incremental effect is extremely dependent on the position(s) of substitution in mono- and dichloro esters and that the variations are considerably reduced with further substitution. If average values are considered, it is apparent that monochlorination results in an increase of 178 retention index units, the values being reduced with increasing degrees of chlorination to 139, 135, 131 and 128 units with di-, tri-, tetra- and penta-substi-

TABLE IV

RETENTION INCREMENTS OF CHLORINE SUBSTITUENTS IN METHYL CHLOROBUTANOATES AT 100°C

Methyl ester	*ΣΔCl*	*Σ1Cl*	*Σ2Cl*	*ΔCl*
Butanoic acid				
2-Chlorobutanoic acid	151	151		151
3-Chlorobutanoic acid	154	154		154
4-Chlorobutanoic acid	223	223		223
2,2-Dichlorobutanoic acid	247		247	124
3,3-Dichlorobutanoic acid	248		248	124
erythro-2,3-Dichlorobutanoic acid	268		268	134
threo-2,3-Dichlorobutanoic acid	299		299	150
4,4-Dichlorobutanoic acid	335		335	168
3,4-Dichlorobutanoic acid	345		345	173
2,4-Dichlorobutanoic acid	346		346	173

tution, respectively. It is apparent that the study is compatible with a recent report by Komárek *et al.*[7] of halogenatedd alkyl propanoates and butanoates. In this work the retentions of methyl propanoate and methyl 2- and 3-chloropropanoates are in agreement and the conclusions of both works are complementary.

Table IV shows the retention increments of methyl chlorobutanoates, and it is apparent that the positional variations increase as before and that the disubstitution produces a lower individual contribution than the monosubstitution, *i.e.*, 176 to 149 units.

The data show that overall the retention increments with both mono- and disubstitution are similar with propanoates and butanoates, monochlorination producing increases of 178 and 176 units with both series and dichlorination increases of 139 and 149 units.

The effects of substitution in the acyl chain extends to the work of Komárek *et al.*[7], who reported that the influence of chlorine or bromine atoms introduced in halogenated propanoates or butanoates had a greater effect as the alkyl chain length was reduced.

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