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GAS-LIQUID CHROMATOGRAPHIC ANALYSES

XVIII*. SEPARATION OF ALIPHATIC C_1 - C_{18} *n*-ALKYL ESTERS OF BUTANOIC, 2-CHLOROBUTANOIC, 3-CHLOROBUTANOIC AND 4-CHLOROBUTANOIC ACIDS WITH THE CORRESPONDING ALCOHOLS

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SUMMARY

The gas chromatography of *n*-alcohols (ROH) and *n*-alkyl butanoates ($CH_3CH_2CH_2COOR$), 2-chlorobutanoates ($CH_3CH_2CHClCOOR$), 3-chlorobutanoates ($CH_3CHClCH_2COOR$) and 4-chlorobutanoates ($CH_2ClCH_2CH_2COOR$), where the alcohol chain length (R) varied between 1 and 18, was studied on SE-30 and OV-351 quartz capillary columns with temperature programming. The separation of a mixture of the above compounds with *n*-tetradecane (76 components in all) was complete on SE-30. Generally, the following compounds are eluted in turn: C_{n+5} -alcohol < C_{n+2} -alkyl butanoate < C_n -alkyl 4-chlorobutanoate < C_{n+1} -alkyl 2-chlorobutanoate < C_{n+1} -alkyl 3-chlorobutanoate ($n \geq 2$). On OV-351, however, four complete and some partial overlappings occurred, the components generally being eluted in the sequence C_{n+4} -alkyl butanoate < C_{n+1} -alkyl 3-chlorobutanoate < C_{n+5} -alcohol < C_n -alkyl 4-chlorobutanoate < C_{n+2} -alkyl 2-chlorobutanoate ($n \geq 3$). With chain lengths of $n = 12$ and 14 4-chloro and 2-chloro esters overlapped, whereas octadecyl 2-chlorobutanoate eluted earlier than hexadecyl 4-chlorobutanoate at $n = 16$.

INTRODUCTION

In Part XVII¹ I dealt with the separation of primary straight-chain C_1 - C_{18} alcohols and their propanoyl, 2-chloropropanoyl and 3-chloropropanoyl derivatives on non-polar and polar capillary columns with temperature programming. SE-30 proved to be more efficient than OV-351, separating the mixture completely.

This paper describes the gas chromatographic (GC) retention behaviour of C_1 - C_{18} *n*-alkyl butanoates and the corresponding monochlorinated isomers. The retention data of the compounds are given relative to the corresponding *n*-alcohols and *n*-tetradecane. The retentions are also expressed as the ratios of the retention

* For Part XVII, see ref. 1.

times of the compounds on OV-351 divided by those on SE-30. The order of elution of the components is discussed.

EXPERIMENTAL

Samples

Primary C_1 - C_{18} alcohols were commercial products (Fluka, Buchs, Switzerland). *n*-Alkyl butanoates and the corresponding monochlorinated isomers were synthesized from aliphatic alcohols and acid chlorides as described earlier². Butanoyl chloride was prepared by the reaction of benzoyl chloride with commercial butanoic acid (Fluka)³, 2-chlorobutanoyl chloride by chlorination of butanoyl chloride⁴ and 3-chlorobutanoyl chloride from the corresponding acid⁵ with thionyl chloride. 4-Chlorobutanoyl chloride was a commercial product (Merck-Schuchardt, F.R.G.) and was used after redistillation.

Gas chromatography

Analyses were performed on a Perkin-Elmer Sigma 3 instrument under the following operating conditions: injector and flame-ionization detector temperatures, 280°C; nitrogen carrier gas flow-rate, 1 ml min⁻¹; splitting ratio, 1:30; and chart speed, 10 mm min⁻¹. The columns used were a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.33 mm I.D.), supplied by SGE (North Melbourne, Australia), and a fused silica OV-351 WCOT column (25 × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The following column temperatures were used: on SE-30, programmed from 50 to 320°C at 6°C min⁻¹; and on OV-351, programmed from 50 to 230°C at 6°C min⁻¹ and held at 230°C until elution of peaks had ceased.

The chromatographic data were analysed with a Hewlett-Packard Model 3390A reporting integrator using standard programs.

RESULTS AND DISCUSSION

The retention data of the compounds studied are presented in Table I. Figs. 1 and 2 give the chromatograms of the mixture analysed on SE-30 and OV-351, respectively.

Fig. 1 shows that complete separation of the individual components could be achieved on a SE-30 capillary column, as previously reported for a mixture of *n*- C_1 - C_{18} alcohols and their propanoyl derivatives¹. Four lower alcohols are eluted earlier than methyl butanoate and six lower alcohols before monochlorinated methyl butanoates. Methyl 2-chloro and 3-chloroisomers are eluted earlier than propyl butanoate, methyl 4-chlorobutanoate appearing between ethyl 2-chloro and 3-chloro isomers. After that the following retention order of the compounds is observed: C_{n+5} -alcohol < C_{n+2} -alkyl butanoate < C_n -alkyl 4-chlorobutanoate < C_{n+1} -alkyl 2-chlorobutanoate < C_{n+1} -alkyl 3-chlorobutanoate ($n \geq 2$).

As shown, *n*-tetradecane is eluted between octyl butanoate and hexyl 4-chlorobutanoate (Fig. 1). Table I shows that on SE-30 the relative retention times, relative to *n*-tetradecane, varied from 0.11 to 1.98. By assigning the retention times relative to the alcohols, it becomes evident (Fig. 3) that the retention is maximized with butyl butanoate (2.83) and propyl 2-, 3- and 4-chlorobutanoate (4.06, 4.18 and 4.80, respectively).

TABLE I

RETENTION DATA FOR PRIMARY C₁-C₁₈ STRAIGHT-CHAIN ALCOHOLS AND THEIR BUTANOYL, 2-CHLOROBUTANOYL, 3-CHLOROBUTANOYL AND 4-CHLOROBUTANOYL DERIVATIVES ON SE-30 AND OV-351 QUARTZ-CAPILLARY COLUMNS

Conditions as in Figs. 1 and 2.

Compound	Column								
	SE-30				OV-351				
	ART*	RRT**	RRT***	RRT [§]	ART*	RRT**	RRT***	RRT [§]	RRT ^{§§}
Methanol	2.43	0.11	1.00	0.53	2.85	0.27	1.00	0.81	1.17
Ethanol	2.70	0.13	1.00	0.44	3.08	0.29	1.00	0.77	1.14
1-Propanol	3.04	0.14	1.00	0.36	3.91	0.37	1.00	0.77	1.29
1-Butanol	3.90	0.18	1.00	0.35	5.31	0.50	1.00	0.79	1.36
1-Pentanol	5.43	0.25	1.00	0.39	7.20	0.68	1.00	0.83	1.33
1-Hexanol	7.65	0.35	1.00	0.47	9.30	0.88	1.00	0.86	1.22
1-Heptanol	10.39	0.48	1.00	0.56	11.54	1.09	1.00	0.88	1.11
1-Octanol	13.19	0.61	1.00	0.63	13.78	1.31	1.00	0.91	1.04
1-Nonanol	15.79	0.73	1.00	0.68	15.80	1.50	1.00	0.92	1.00
1-Decanol	18.23	0.85	1.00	0.72	17.74	1.68	1.00	0.93	0.97
1-Undecanol	20.59	0.95	1.00	0.76	19.67	1.87	1.00	0.94	0.96
1-Dodecanol	22.81	1.06	1.00	0.78	21.50	2.04	1.00	0.95	0.94
1-Tetradecanol	26.94	1.25	1.00	0.82	24.97	2.37	1.00	0.95	0.93
1-Hexadecanol	30.80	1.43	1.00	0.86	28.20	2.68	1.00	0.96	0.92
1-Octadecanol	34.28	1.59	1.00	0.88	31.41	2.98	1.00	0.96	0.92
Methyl butanoate	4.61	0.21	1.90	1.00	3.50	0.33	1.23	1.00	0.76
Ethyl butanoate	6.09	0.28	2.26	1.00	4.00	0.38	1.30	1.00	0.66
Propyl butanoate	8.40	0.39	2.76	1.00	5.11	0.48	1.31	1.00	0.61
Butyl butanoate	11.05	0.51	2.83	1.00	6.71	0.64	1.26	1.00	0.61
Pentyl butanoate	13.79	0.64	2.54	1.00	8.69	0.82	1.21	1.00	0.63
Hexyl butanoate	16.29	0.76	2.13	1.00	10.84	1.03	1.17	1.00	0.67
Heptyl butanoate	18.65	0.86	1.79	1.00	13.05	1.24	1.13	1.00	0.70
Octyl butanoate	20.90	0.97	1.58	1.00	15.11	1.43	1.10	1.00	0.72
Nonyl butanoate	23.10	1.07	1.46	1.00	17.11	1.62	1.08	1.00	0.74
Decyl butanoate	25.15	1.17	1.38	1.00	19.04	1.81	1.07	1.00	0.76
Undecyl butanoate	27.14	1.26	1.32	1.00	20.91	1.98	1.06	1.00	0.77
Dodecyl butanoate	29.07	1.35	1.27	1.00	22.71	2.15	1.06	1.00	0.78
Tetradecyl butanoate	32.69	1.52	1.21	1.00	26.15	2.48	1.05	1.00	0.80
Hexadecyl butanoate	35.97	1.67	1.17	1.00	29.30	2.78	1.04	1.00	0.81
Octadecyl butanoate	39.05	1.81	1.14	1.00	32.64	3.10	1.04	1.00	0.84
Methyl 2-chlorobutanoate	7.80	0.36	3.21	1.69	7.80	0.74	2.74	2.23	1.00
Ethyl 2-chlorobutanoate	9.70	0.45	3.59	1.59	8.48	0.80	2.75	2.12	0.87
Propyl 2-chlorobutanoate	12.34	0.57	4.06	1.47	10.16	0.96	2.60	1.99	0.82
Butyl 2-chlorobutanoate	14.92	0.69	3.83	1.35	12.19	1.16	2.30	1.82	0.82
Pentyl 2-chlorobutanoate	17.38	0.81	3.20	1.26	14.22	1.35	1.98	1.64	0.82
Hexyl 2-chlorobutanoate	19.71	0.91	2.58	1.21	16.20	1.54	1.74	1.49	0.82
Heptyl 2-chlorobutanoate	21.96	1.02	2.11	1.18	18.16	1.72	1.57	1.39	0.83
Octyl 2-chlorobutanoate	24.11	1.12	1.83	1.15	20.05	1.90	1.46	1.33	0.83
Nonyl 2-chlorobutanoate	26.20	1.21	1.66	1.13	21.91	2.08	1.39	1.28	0.84

(Continued on p. 440)

TABLE I (continued)

Compound	Column								
	SE-30				OV-351				
	ART*	RRT**	RRT***	RRT§	ART*	RRT**	RRT***	RRT§	RRT§§
Decyl 2-chlorobutanoate	28.15	1.31	1.54	1.12	23.70	2.25	1.34	1.24	0.84
Undecyl 2-chlorobutanoate	30.09	1.39	1.46	1.11	25.42	2.41	1.29	1.22	0.84
Dodecyl 2-chlorobutanoate	31.90	1.48	1.40	1.10	27.10	2.57	1.26	1.19	0.85
Tetradecyl 2-chlorobutanoate	35.30	1.64	1.31	1.08	30.29	2.87	1.21	1.16	0.86
Hexadecyl 2-chlorobutanoate	38.46	1.78	1.25	1.07	33.98	3.22	1.20	1.16	0.88
Octadecyl 2-chlorobutanoate	41.37	1.92	1.21	1.06	39.18	3.72	1.25	1.20	0.95
Methyl 3-chlorobutanoate	7.95	0.37	3.27	1.72	8.69	0.82	3.05	2.48	1.09
Ethyl 3-chlorobutanoate	10.01	0.46	3.71	1.64	9.55	0.91	3.10	2.39	0.95
Propyl 3-chlorobutanoate	12.72	0.59	4.18	1.51	11.42	1.08	2.92	2.23	0.90
Butyl 3-chlorobutanoate	15.30	0.71	3.92	1.38	13.50	1.28	2.54	2.01	0.88
Pentyl 3-chlorobutanoate	17.75	0.82	3.27	1.29	15.49	1.47	2.15	1.78	0.87
Hexyl 3-chlorobutanoate	20.09	0.93	2.63	1.23	17.45	1.66	1.88	1.61	0.87
Heptyl 3-chlorobutanoate	22.31	1.03	2.15	1.20	19.38	1.84	1.68	1.49	0.87
Octyl 3-chlorobutanoate	24.46	1.13	1.85	1.17	21.22	2.01	1.54	1.40	0.87
Nonyl 3-chlorobutanoate	26.51	1.23	1.68	1.15	23.05	2.19	1.46	1.35	0.87
Decyl 3-chlorobutanoate	28.46	1.32	1.56	1.13	24.80	2.35	1.40	1.30	0.87
Undecyl 3-chlorobutanoate	30.37	1.41	1.47	1.12	26.50	2.51	1.35	1.27	0.87
Dodecyl 3-chlorobutanoate	32.19	1.49	1.41	1.11	28.12	2.67	1.31	1.24	0.87
Tetradecyl 3-chlorobutanoate	35.56	1.65	1.32	1.09	31.36	2.98	1.26	1.20	0.88
Hexadecyl 3-chlorobutanoate	38.71	1.79	1.26	1.08	35.43	3.36	1.26	1.21	0.92
Octadecyl 3-chlorobutanoate	41.60	1.93	1.21	1.07	41.42	3.93	1.32	1.27	1.00
Methyl 4-chlorobutanoate	9.80	0.45	4.03	2.13	11.29	1.07	3.96	3.23	1.15
Ethyl 4-chlorobutanoate	11.92	0.55	4.41	1.96	12.19	1.16	3.96	3.05	1.02
Propyl 4-chlorobutanoate	14.60	0.68	4.80	1.74	14.05	1.33	3.59	2.75	0.96
Butyl 4-chlorobutanoate	17.06	0.79	4.37	1.54	16.01	1.52	3.02	2.39	0.94
Pentyl 4-chlorobutanoate	19.41	0.90	3.57	1.41	17.99	1.71	2.50	2.07	0.93
Hexyl 4-chlorobutanoate	21.69	1.01	2.84	1.33	19.89	1.89	2.14	1.83	0.92
Heptyl 4-chlorobutanoate	23.89	1.11	2.30	1.28	21.76	2.06	1.89	1.67	0.91
Octyl 4-chlorobutanoate	25.95	1.20	1.97	1.24	23.59	2.24	1.71	1.56	0.91
Nonyl 4-chlorobutanoate	27.95	1.30	1.77	1.21	25.35	2.41	1.61	1.48	0.91
Decyl 4-chlorobutanoate	29.88	1.39	1.64	1.19	27.04	2.57	1.52	1.42	0.90
Undecyl 4-chlorobutanoate	31.72	1.47	1.54	1.17	28.69	2.72	1.46	1.37	0.90
Dodecyl 4-chlorobutanoate	33.48	1.55	1.47	1.15	30.29	2.87	1.41	1.33	0.90
Tetradecyl 4-chlorobutanoate	36.77	1.70	1.36	1.12	33.98	3.22	1.36	1.30	0.92
Hexadecyl 4-chlorobutanoate	39.82	1.85	1.29	1.11	39.28	3.73	1.39	1.34	0.99
Octadecyl 4-chlorobutanoate	42.65	1.98	1.24	1.09	47.62	4.52	1.52	1.46	1.12
<i>n</i> -Tetradecane	21.57	1.00	0.80	0.66	10.54	1.00	0.42	0.40	0.49

* Absolute retention times (min) were measured from sample injection (Figs. 1 and 2).

** Relative retention time for *n*-tetradecane taken as 1.00.

*** Relative retention time for the corresponding *n*-alcohol taken as 1.00.

§ Relative retention time for the corresponding *n*-alkyl butanoate taken as 1.00.

§§ Relative retention time for the corresponding compound on SE-30 taken as 1.00.

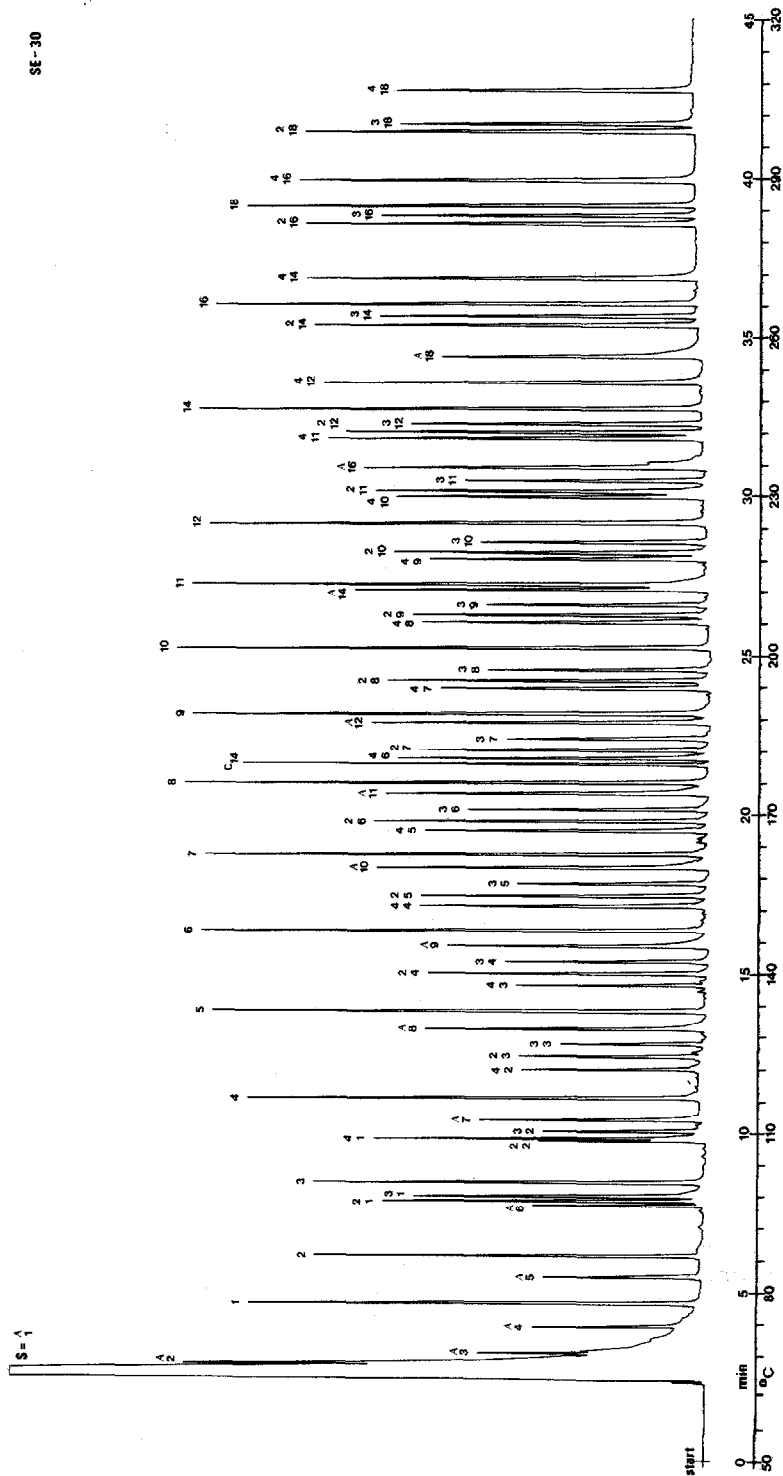


Fig. 1. Chromatogram of a mixture of primary C_1-C_{18} straight-chain alcohols ($\bar{1}-\bar{18}$) and the corresponding *n*-alkyl butanoates ($\bar{1}-\bar{18}$), 2-chlorobutanoates ($\bar{1}-\bar{18}$), 3-chlorobutanoates ($\bar{1}-\bar{18}$) and 4-chlorobutanoates ($\bar{1}-\bar{18}$) on SE-30. Methanol ($\bar{1}$) = solvent; C_{14} = *n*-tetradecane; the upper number indicates the position of the chloro substituent; A = alcohol; the lower number represents the chain length.

OV-351

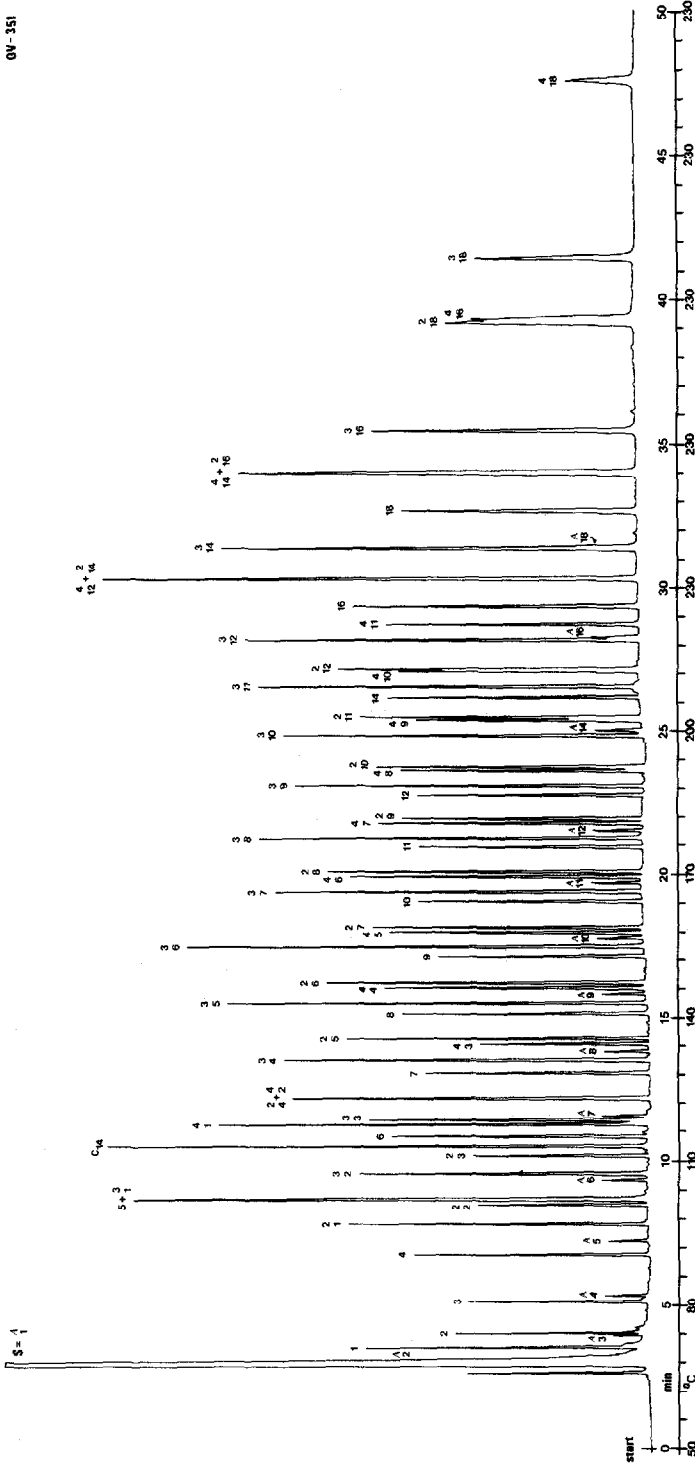


Fig. 2. Chromatogram of the mixture in Fig. 1 on OV-351.

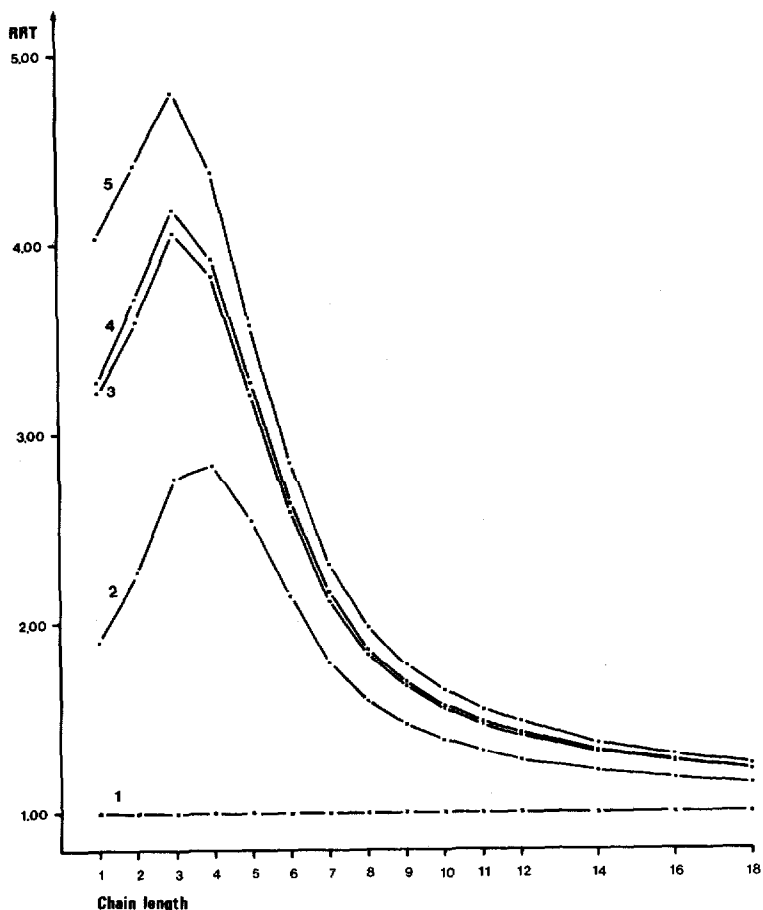


Fig. 3. Relative retention times (RRTs) for C_1 - C_{18} *n*-alkyl butanoates (curve 2), 2-chlorobutanoates (curve 3), 3-chlorobutanoates (curve 4) and 4-chlorobutanoates (curve 5) on SE-30. Relative retention times for the corresponding *n*-alcohols (curve 1) taken as 1.00 (Table I).

Fig. 2 shows the separation of the mixture on a highly polar OV-351 capillary column. As can be seen, the following compounds overlapped completely: pentyl butanoate with methyl 3-chlorobutanoate, ethyl 4-chlorobutanoate with butyl 2-chlorobutanoate, dodecyl 4-chlorobutanoate with tetradecyl 2-chlorobutanoate and tetradecyl 4-chlorobutanoate with hexadecyl 2-chlorobutanoate. In addition, some partial overlappings are also observed, as is evident in Fig. 2.

Two lower alcohols are eluted earlier than methyl butanoate, butyl butanoate and 1-pentanol appearing before methyl 2-chlorobutanoate. As a consequence of the relatively long retention times of the ω -chloro isomers, methyl 4-chlorobutanoate is eluted between hexyl butanoate and propyl 3-chlorobutanoate. Generally, the following compounds are eluted in turn: C_{n+4} -alkyl butanoate < C_{n+1} -alkyl 3-chlorobutanoate < C_{n+5} -alcohol < C_n -alkyl 4-chlorobutanoate < C_{n+2} -alkyl 2-chlorobutanoate ($n \geq 3$). The compounds are eluted closer together with increasing chain length, partial overlapping of dodecyl 3-chlorobutanoate with 1-hexadecanol and of

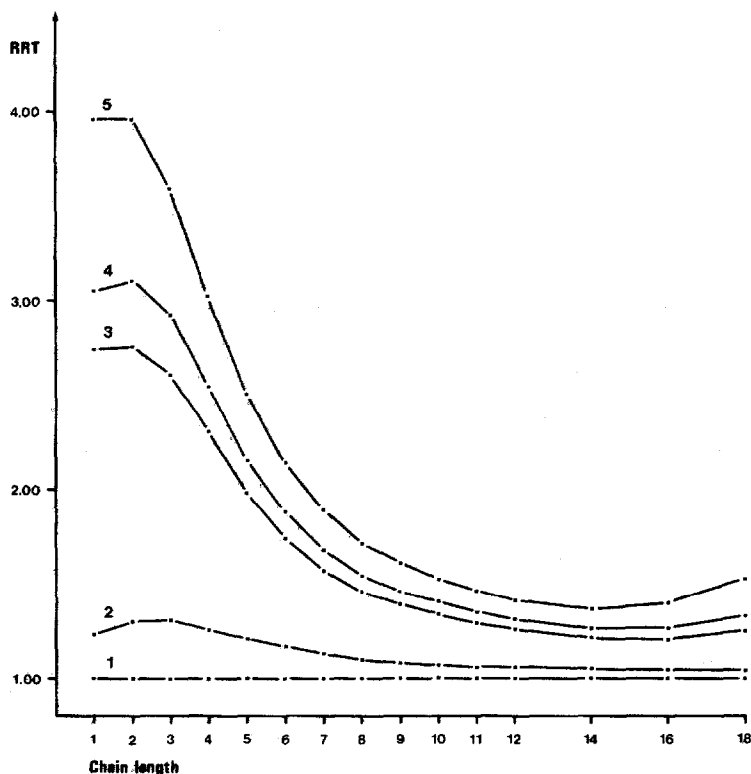


Fig. 4. Relative retention times (RRTs) for C_1 - C_{18} *n*-alkyl butanoates (curve 2), 2-chlorobutanoates (curve 3), 3-chlorobutanoates (curve 4) and 4-chlorobutanoates (curve 5) on OV-351. Relative retention times for the corresponding *n*-alcohols (curve 1) taken as 1.00 (Table I).

tetradecyl 3-chlorobutanoate with 1-octadecanol being detected. Additional overlappings occurred with the 4-chloro and 2-chloro isomers ($n \geq 8$), the order of elution of the compounds ($n \geq 12$) not being in accordance with that given above, *i.e.*, with chain lengths of $n = 12$ and 14, the isomers are coincident and octadecyl 2-chlorobutanoate eluted slightly earlier than hexadecyl 4-chlorobutanoate ($n = 16$), as shown in Fig. 2.

The retention times relative to *n*-tetradecane varied from 0.27 to 4.52 (Table I), being clearly higher than those observed on SE-30. Fig. 4 shows that lower retention times relative to the alcohols on a polar column are observed. Retention is maximized within propyl butanoate (1.31), ethyl 2-chlorobutanoate (2.75), ethyl 3-chlorobutanoate (3.10) and methyl and ethyl 4-chlorobutanoate (3.96).

Fig. 5 and Table I show that under the same operating conditions, only the methyl 3-chloro isomer and the methyl and ethyl 4-chloro isomers showed greater retention times on OV-351 in addition to the lower alcohols, methyl 2-chlorobutanoate appearing at the same time on both columns.

By comparing the results given here with those reported earlier¹, the following retention order for *n*-alkyl propanoates and butanoates on SE-30 is observed: propanoate < butanoate < 2-chloropropanoate < 3-chloropropanoate < 2-chloro-

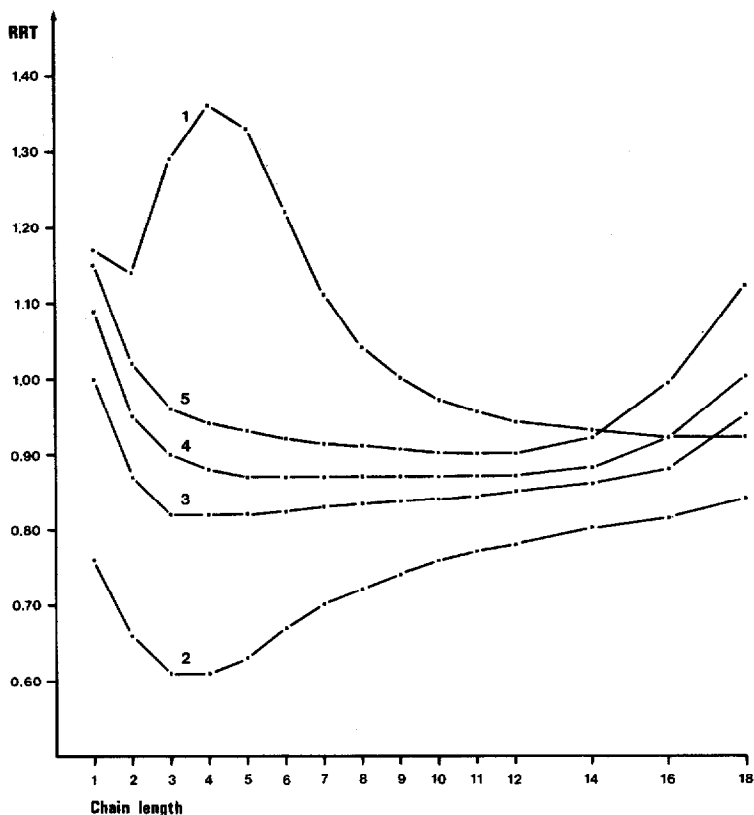


Fig. 5. Relative retention times (RRTs) for C_1 - C_{18} *n*-alcohols (curve 1), *n*-alkyl butanoates (curve 2), 2-chlorobutanoates (curve 3), 3-chlorobutanoates (curve 4) and 4-chlorobutanoates (curve 5) on OV-351. Relative retention times for the corresponding compounds on SE-30 taken as 1.00 (Table I).

butanoate < 3-chlorobutanoate < 4-chlorobutanoate. On OV-351, however, the ω -chloro isomers are eluted in turn, the sequence being propanoate < butanoate < 2-chloropropanoate < 2-chlorobutanoate < 3-chlorobutanoate < 3-chloropropanoate < 4-chlorobutanoate. As previously reported⁶⁻⁹, methyl chloroacetate is eluted on SE-30 earlier than methyl 2-chloropropanoate, the compounds being eluted in the reverse order on a polar column. The retention behaviour of C_2 - C_8 *n*-alkyl chloroacetates¹⁰ and the corresponding 2-chloropropanoates¹ indicates the same phenomenon with higher esters also.

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