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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XXII*. PRIMARY C_8–C_{18} STRAIGHT-CHAIN ALKANOLS AND THE CORRESPONDING ALKYL ESTERS OF ACETIC, MONOCHLOROACETIC, DICHLOROACETIC AND TRICHLOROACETIC ACIDS

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SUMMARY

Programmed and isothermal capillary gas chromatography of primary straight-chain C_8–C_{12}, C_{14}, C_{16} and C_{18} alkanols and the corresponding *n*-alkyl acetates, monochloroacetates, dichloroacetates and trichloroacetates has been studied on SE-30 and OV-351 capillary columns. A non-polar column gave 38 peaks for a mixture of 40 individual components, the retention order being C_{n+5}-alkanol < C_n-alkyl trichloroacetate < C_{n+1}-alkyl dichloroacetate < C_{n+4}-alkyl acetate < C_{n+2}-alkyl monochloroacetate. A poorer resolution of a mixture with two reversed elution sequences on a polar column was achieved, the components being eluted in the order C_n-alkyl monochloroacetate < C_{n+4}-alkyl acetate < C_n-alkyl trichloroacetate < C_n-alkyl dichloroacetate < C_{n+4}-alkanol.

INTRODUCTION

Previously, the gas chromatographic (GC) separation of lower (C_1–C_8) *n*-alkyl esters of acetic, monochloroacetic, dichloroacetic and trichloroacetic acids has been investigated[1], using temperature programming and capillary columns coated with SE-30, Carbowax 20M and OV-351. The retention indices and the effect of retention index increments of the same four homologous series of esters on non-polar (SE-30) and highly polar (OV-351) stationary phases at increasing temperatures have also been reported[2]. Komárek *et al.*[3] studied the separation of mixtures of homologous series of C_1–C_{16} *n*-alkyl and C_3–C_5 isoalkyl acetates, monochloroacetates, dichloroacetates, trichloroacetates, monobromoacetates, monoiodoacetates and trifluoroacetates on a capillary column coated with the non-polar stationary phase OV-101. Retention indices and increments of retention indices were used to correlate the type and number of halogens in the acid moiety of the ester molecule[3].

This work extends previous GC studies on acetic acid derivatives[1–7] and on the

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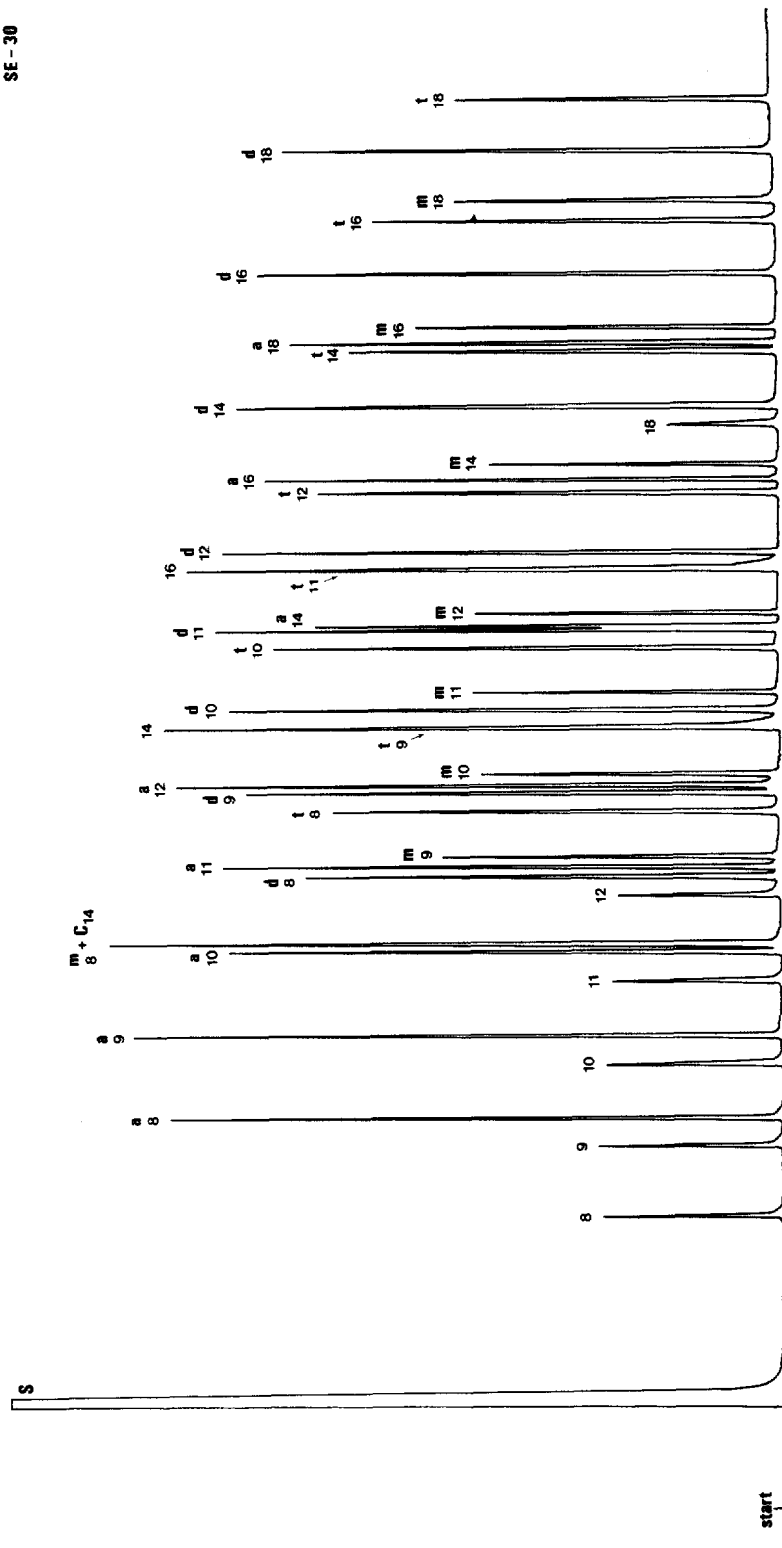

Fig. 1. Chromatogram of a mixture of primary C_8–C_{18} straight-chain alkanols (8–18) and the corresponding *n*-alkyl acetates (a8–a18), monochloroacetates (m8–m18), dichloroacetates (d8–d18) and trichloroacetates (t8–t18), analysed on SE-30 with temperature programming. S = Solvent; C_{14} = *n*-tetradecane.

propanoyl and monochloropropanoyl[8] and butanoyl and monochlorobutanoyl[9] derivatives of primary straight-chain alkanols by showing the retention behaviour of C_8–C_{18} *n*-alkanols and the corresponding *n*-alkyl acetates, monochloroacetates, dichloroacetates and trichloroacetates. A mixture of the compounds was separated on SE-30 and OV-351 capillary columns using temperature-programmed and isothermal operating conditions. The retention data are given and the elution order is discussed.

EXPERIMENTAL

Apparatus

Separations were carried out on a Perkin-Elmer Sigma 3 gas chromatograph under the following operating conditions: injection and flame-ionization detection (FID) temperatures, 275°C; carrier gas (nitrogen) flow-rate, 1 ml min^{-1}; splitting ratio, 1:20; and chart speed, 10 mm min^{-1}. The columns used were a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.30 mm I.D.), supplied by SGE (North Melbourne, Australia), and a fused-silica OV-351 WCOT column (25 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The column temperature was programmed on SE-30 from 100 to 310°C at 6°C min^{-1} and on OV-351 from 100 to 230°C at 6°C min^{-1} and held at the final temperature until elution of peaks had ceased. The isothermal data were analysed at 200°C.

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

Samples

The alkanols (8–18) were commercial products (Fluka, Buchs, Switzerland). *n*-Alkyl acetates (a8–a18), monochloroacetates (m8–m18), dichloroacetates (d8–d18) and trichloroacetates (t8–t18) were prepared from the corresponding alkanols and acid chlorides as described earlier[10]; acetyl chloride (Fluka) and trichloroacetyl chloride (Merck-Schuchardt, Darmstadt, F.R.G.) were commercial products and monochloroacetyl and dichloroacetyl chloride were obtained by the reaction of thionyl chloride (Fluka) with the commercial acids (Fluka). The commercial mixtures of *n*-alkanes analysed originated from different sources.

A mixture of GC-pure individual components was used for GC analyses.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the separations of the four series of compounds studied, obtained on SE-30 and OV-351 with temperature programming. The corresponding retention data are presented in Table I and Table II gives the isothermal data for the compounds. Plots of the data are illustrated in Figs. 3–6.

As shown previously with the lower homologous alkyl esters[1], the best separation occurred on SE-30 (Fig. 1). All the esters (a8–a18, m8–m18, d8–d18 and t8–t18) were resolved, whereas the peaks of the alkanols (14 and 16) were overlapped by those of alkyl trichloroacetates (t9 and t11, respectively). The order of elution of the individual components in the mixture from SE-30 was C_{n+5}-alkanol < C_n-alkyl trichloroacetate < C_{n+1}-alkyl dichloroacetate < C_{n+4}-alkyl acetate < C_{n+2}-alkyl monochloroacetate. The compounds were eluted in the same order also under iso-

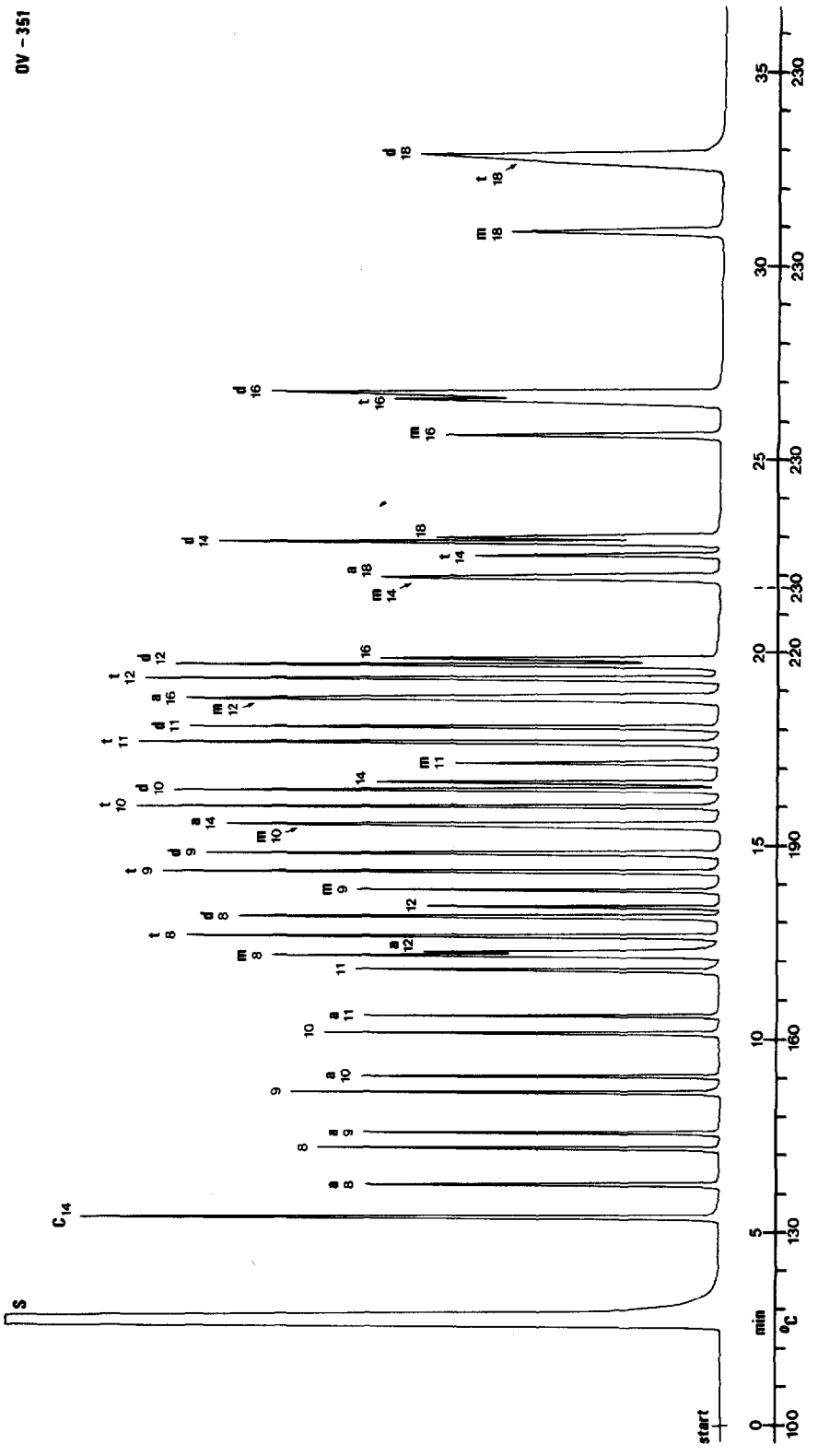

Fig. 2. Chromatogram of the same mixture as in Fig. 1, obtained on OV-351.

thermal conditions, the elution sequence of the esters being the same as reported previously by Komárek *et al.*[3] using an OV-101 capillary column at 200°C.

Fig. 2 shows that the use of a polar column results in more overlapping peaks, *i.e.*, alkyl monochloroacetates (m10, m12 and m14) with alkyl acetates (a14, a16 and a18, respectively), and octadecyl trichloroacetate (t18) with the corresponding dichloro isomer (d18). The use of the relatively low maximum temperature (230°C) recommended for the highly polar OV-351 stationary phase led to peak broadening of the long-chain isomers under the isothermal operating conditions after reaching the final temperature (Fig. 2). The polar column used also seemed to be unsuitable, particularly for the long-chain trichloro isomers, the FID response of which decreasing strongly, especially under isothermal conditions at high temperatures. The same effect has been previously reported for the long-chain chloro esters of acetic acid, analysed on OV-351[7]. The reversed elution order between the alcohols and alkyl acetates and between the dichloro and trichloro isomers occurred on a polar column, the retention order being C_n-alkyl monochloroacetate < C_{n+4}-alkyl acetate < C_n-alkyl trichloroacetate < C_n-alkyl dichloroacetate < C_{n+4}-alkanol.

Figs. 3 and 4 show the plots for the five homologous series, together with *n*-alkanes, determined using temperature programming. The series were eluted on SE-30 (Fig. 3) and OV-351 (Fig. 4) between the following *n*-alkanes, respectively: alkanols (curve 1) C_{10}–C_{21}, C_{15}–C_{26}; alkyl acetates (curve 2) C_{11}–C_{23}, C_{14}–C_{25}; alkyl monochloroacetates (curve 3) C_{14}–C_{25}, C_{18}–C_{30}; alkyl dichloroacetates (curve 4) C_{14}–C_{26}, C_{19}–C_{30}; and alkyl trichloroacetates (curve 5) C_{15}–C_{27}, C_{19}–C_{30}. The approximate retention indices determined based on the data given in Fig. 3, *e.g.*, for octyl esters (a8, m8, d8 and t8), with the values of Komárek *et al.*[3] determined on OV-101 at 200°C in parentheses, are as follows: octyl acetate 1188 (1189.4), octyl monochloroacetate 1400 (1406.0), octyl dichloroacetate 1482 (1484.3) and octyl trichloroacetate 1560 (1563.8). The other series also show the same exceptional agreement, although the analyses were carried out with different stationary phases, under different operating conditions and the data in this work were not corrected for the dead volume. However, the disparities between the retention indices of the higher esters increase owing to the effect of temperature, as shown for the hexadecyl isomers eluted at high temperature: acetate 1998 (1991.1), monochloroacetate 2227 (2209.8), dichloroacetate 2313 (2287.0) and trichloroacetate 2400 (2364.9). Also the values 1468 (1478), 1876 (1881), 1941 (1941) and 1910 (1910) for the octyl esters (a8, m8, d8 and t8) obtained on OV-351 are in good agreement with the retention indices determined on the same column at 140°C by Haken *et al.*[2] given in parentheses.

Plots of the relative retention times of the compounds, relative to *n*-alkanols, are given in Figs. 5 and 6, determined under temperature-programmed and isothermal conditions. As shown, higher retention times are always observed on SE-30, if the data for some of the higher homologues on OV-351 are omitted as elution occurred under isothermal conditions rather than with temperature programming (Figs. 2, 4 and 5). A significant enhancement of retention for the alkyl acetates (curve 2) compared with the free alkanols (curve 1) was found on SE-30, whereas a reduction in retention occurred on OV-351. As reported previously[8], the C_5–C_{18} *n*-alkyl propanoates are also eluted earlier than the alkanols on a polar column, whereas all *n*-alkyl butanoates had higher retentions on OV-351[9].

The effects of the various chlorine substituents in the individual homologous

TABLE I

RETENTION DATA FOR C_8–C_{18} *n*-ALKANOLS AND C_8–C_{18} *n*-ALKYL ACETATES, MONOCHLOROACETATES, DICHLOROACETATES AND TRICHLOROACETATES, MEASURED ON SE-30 AND OV-351 WITH TEMPERATURE PROGRAMMING

Conditions as in Figs. 1 and 2.

Peak	*Compound*	*Column*								
		SE-30				*OV-351*				
		*ART***	*RRT****	*RRT*****	*RRT*\$*	*ART***	*RRT****	*RRT*****	*RRT*\$*	*RRT*\$\$*
8	1-Octanol	7.03	0.52	1.00	0.75	7.18	1.33	1.00	1.16	1.02
9	1-Nonanol	8.72	0.64	1.00	0.77	8.61	1.59	1.00	1.14	0.99
10	1-Decanol	10.67	0.79	1.00	0.80	10.19	1.89	1.00	1.13	0.96
11	1-Undecanol	12.65	0.93	1.00	0.82	11.79	2.18	1.00	1.11	0.93
12	1-Dodecanol	14.72	1.08	1.00	0.85	13.41	2.48	1.00	1.09	0.91
14	1-Tetradecanol	18.71	1.38	1.00	0.88	16.70	3.09	1.00	1.07	0.89
16	1-Hexadecanol	22.53	1.66	1.00	0.91	19.89	3.68	1.00	1.06	0.88
18	1-Octadecanol	25.99	1.91	1.00	0.93	23.01	4.26	1.00	1.05	0.89
a8	Octyl acetate	9.40	0.69	1.34	1.00	6.21	1.15	0.86	1.00	0.66
a9	Nonyl acetate	11.36	0.84	1.30	1.00	7.52	1.39	0.87	1.00	0.66
a10	Decyl acetate	13.38	0.99	1.25	1.00	9.00	1.67	0.88	1.00	0.67
a11	Undecyl acetate	15.39	1.13	1.22	1.00	10.60	1.96	0.90	1.00	0.69
a12	Dodecyl acetate	17.36	1.28	1.18	1.00	12.26	2.27	0.91	1.00	0.71
a14	Tetradecyl acetate	21.15	1.56	1.13	1.00	15.56	2.88	0.93	1.00	0.74
a16	Hexadecyl acetate	24.70	1.82	1.10	1.00	18.85	3.49	0.95	1.00	0.76
a18	Octadecyl acetate	27.94	2.06	1.08	1.00	22.00	4.07	0.96	1.00	0.79

m8	Octyl monochloroacetate	13.59	1.00	1.93	1.45	12.18	2.26	1.70	1.96	0.90
m9	Nonyl monochloroacetate	15.63	1.15	1.79	1.38	13.82	2.56	1.61	1.84	0.88
m10	Decyl monochloroacetate	17.61	1.30	1.65	1.32	15.54	2.88	1.53	1.73	0.88
m11	Undecyl monochloroacetate	19.56	1.44	1.55	1.27	17.17	3.18	1.46	1.62	0.88
m12	Dodecyl monochloroacetate	21.46	1.58	1.46	1.24	18.82	3.49	1.40	1.54	0.88
m14	Tetradecyl monochloroacetate	25.02	1.84	1.34	1.18	21.95	4.06	1.31	1.41	0.88
m16	Hexadecyl monochloroacetate	28.29	2.08	1.26	1.15	25.70	4.76	1.29	1.36	0.91
m18	Octadecyl monochloroacetate	31.32	2.31	1.21	1.12	31.03	5.75	1.35	1.41	0.99
d8	Octyl dichloroacetate	15.16	1.12	2.16	1.61	13.20	2.44	1.84	2.13	0.87
d9	Nonyl dichloroacetate	17.19	1.27	1.97	1.51	14.83	2.75	1.72	1.97	0.86
d10	Decyl dichloroacetate	19.15	1.41	1.79	1.43	16.50	3.06	1.62	1.83	0.86
d11	Undecyl dichloroacetate	21.06	1.55	1.66	1.37	18.12	3.36	1.54	1.71	0.86
d12	Dodecyl dichloroacetate	22.92	1.69	1.56	1.32	19.74	3.66	1.47	1.61	0.86
d14	Tetradecyl dichloroacetate	26.40	1.94	1.41	1.25	22.94	4.25	1.37	1.47	0.87
d16	Hexadecyl dichloroacetate	29.59	2.18	1.31	1.20	26.77	4.96	1.35	1.42	0.90
d18	Octadecyl dichloroacetate	32.58	2.40	1.25	1.17	32.90	6.09	1.43	1.50	1.01
t8	Octyl trichloroacetate	16.72	1.23	2.38	1.78	12.70	2.35	1.77	2.05	0.76
t9	Nonyl trichloroacetate	18.70	1.38	2.14	1.65	14.38	2.66	1.67	1.91	0.77
t10	Decyl trichloroacetate	20.65	1.52	1.94	1.54	16.05	2.97	1.58	1.78	0.78
t11	Undecyl trichloroacetate	22.50	1.66	1.78	1.46	17.71	3.28	1.50	1.67	0.79
t12	Dodecyl trichloroacetate	24.37	1.79	1.66	1.40	19.36	3.59	1.44	1.58	0.79
t14	Tetradecyl trichloroacetate	27.73	2.04	1.48	1.31	22.53	4.17	1.35	1.45	0.81
t16	Hexadecyl trichloroacetate	30.86	2.27	1.37	1.25	26.61	4.93	1.34	1.41	0.86
t18	Octadecyl trichloroacetate	33.75	2.49	1.30	1.21	32.71	6.06	1.42	1.49	0.97
C14	*n*-Tetradecane	13.58	1.00	0.73	0.64	5.40	1.00	0.32	0.35	0.40

* Absolute retention times (min) were measured from sample injection (Figs. 1 and 2).
** Relative retention time for *n*-tetradecane (C14) taken as 1.00.
*** Relative retention time for the corresponding *n*-alkanol (8–18) taken as 1.00.
§ Relative retention time for the corresponding *n*-alkyl acetate (a8–a18) taken as 1.00.
§§ Relative retention time for the compound on SE-30 taken as 1.00.

TABLE II

RETENTION DATA FOR C_8–C_{18} *n*-ALKANOLS AND C_8–C_{18} *n*-ALKYL ACETATES, MONOCHLOROACETATES, DICHLOROACETATES AND TRICHLOROACETATES, MEASURED ON SE-30 AND OV-351 AT 200°C

Peak	*Compound*	*Column*								
		SE-30				*OV-351*				
		*ART**	*RRT***	*RRT****	*RRT*§	*ART**	*RRT***	*RRT****	*RRT*§	*RRT*§§
8	1-Octanol	3.57	0.72	1.00	0.90	3.24	1.08	1.00	1.02	0.91
9	1-Nonanol	3.81	0.76	1.00	0.90	3.44	1.14	1.00	1.03	0.90
10	1-Decanol	4.19	0.84	1.00	0.87	3.70	1.23	1.00	1.04	0.88
11	1-Undecanol	4.74	0.95	1.00	0.84	4.04	1.34	1.00	1.05	0.85
12	1-Dodecanol	5.52	1.11	1.00	0.80	4.50	1.50	1.00	1.06	0.82
14	1-Tetradecanol	8.23	1.65	1.00	0.75	6.02	2.00	1.00	1.09	0.73
16	1-Hexadecanol	13.58	2.72	1.00	0.71	8.95	2.97	1.00	1.15	0.66
18	1-Octadecanol	24.40	4.89	1.00	0.70	14.32	4.76	1.00	1.17	0.59
a8	Octyl acetate	3.97	0.80	1.11	1.00	3.17	1.05	0.98	1.00	0.80
a9	Nonyl acetate	4.25	0.85	1.12	1.00	3.34	1.11	0.97	1.00	0.79
a10	Decyl acetate	4.81	0.96	1.15	1.00	3.56	1.18	0.96	1.00	0.74
a11	Undecyl acetate	5.65	1.13	1.19	1.00	3.85	1.28	0.95	1.00	0.68
a12	Dodecyl acetate	6.89	1.38	1.25	1.00	4.23	1.41	0.94	1.00	0.61
a14	Tetradecyl acetate	10.96	2.20	1.33	1.00	5.50	1.83	0.91	1.00	0.50
a16	Hexadecyl acetate	19.10	3.83	1.41	1.00	7.80	2.59	0.87	1.00	0.41
a18	Octadecyl acetate	35.03	7.02	1.44	1.00	12.26	4.07	0.86	1.00	0.35

m8	Octyl monochloroacetate	5.00	1.00	1.40	1.26	4.23	1.41	1.31	1.33	0.85
m9	Nonyl monochloroacetate	5.90	1.18	1.55	1.39	4.72	1.57	1.37	1.41	0.80
m10	Decyl monochloroacetate	7.18	1.44	1.71	1.49	5.44	1.81	1.47	1.53	0.76
m11	Undecyl monochloroacetate	8.94	1.79	1.89	1.58	6.42	2.13	1.59	1.67	0.72
m12	Dodecyl monochloroacetate	11.50	2.30	2.08	1.67	7.73	2.57	1.72	1.83	0.67
m14	Tetradecyl monochloroacetate	20.12	4.03	2.44	1.84	12.06	4.01	2.00	2.19	0.60
m16	Hexadecyl monochloroacetate	37.35	7.48	2.75	1.96	20.35	6.76	2.27	2.61	0.54
m18	Octadecyl monochloroacetate	71.30	14.29	2.92	2.04	35.95	11.94	2.51	2.93	0.50
d8	Octyl dichloroacetate	5.65	1.13	1.58	1.42	4.51	1.50	1.39	1.42	0.80
d9	Nonyl dichloroacetate	6.88	1.38	1.81	1.62	5.13	1.70	1.49	1.54	0.75
d10	Decyl dichloroacetate	8.54	1.71	2.04	1.78	6.00	1.99	1.62	1.69	0.70
d11	Undecyl dichloroacetate	10.93	2.19	2.31	1.93	7.16	2.38	1.77	1.86	0.66
d12	Dodecyl dichloroacetate	14.28	2.86	2.59	2.07	8.80	2.92	1.96	2.08	0.62
d14	Tetradecyl dichloroacetate	25.61	5.13	3.11	2.34	14.10	4.68	2.34	2.56	0.55
d16	Hexadecyl dichloroacetate	48.15	9.85	3.55	2.52	24.10	8.01	2.69	3.09	0.50
d18	Octadecyl dichloroacetate	92.40	18.52	3.79	2.64	42.40	14.09	2.96	3.46	0.46
t8	Octyl trichloroacetate	6.62	1.33	1.85	1.67	4.41	1.47	1.36	1.39	0.67
t9	Nonyl trichloroacetate	8.18	1.64	2.15	1.92	5.00	1.66	1.45	1.50	0.61
t10	Decyl trichloroacetate	10.39	2.08	2.48	2.16	5.80	1.93	1.57	1.63	0.56
t11	Undecyl trichloroacetate	13.50	2.71	2.85	2.39	6.89	2.29	1.71	1.79	0.51
t12	Dodecyl trichloroacetate	17.82	3.57	3.23	2.59	8.41	2.79	1.87	1.99	0.47
t14	Tetradecyl trichloroacetate	32.73	6.56	3.98	3.08	13.19	4.38	2.19	2.40	0.40
t16	Hexadecyl trichloroacetate	62.05	12.43	4.57	3.25	22.55	7.49	2.52	2.89	0.36
t18	Octadecyl trichloroacetate	119.50	23.95	4.90	3.41	39.95	13.27	2.79	3.26	0.33
C14	*n*-Tetradecane	4.99	1.00	0.61	0.46	3.01	1.00	0.50	0.55	0.60

* Absolute retention times (min) were measured from sample injection.
** Relative retention time for *n*-tetradecane (C14) taken as 1.00.
*** Relative retention time for the corresponding *n*-alkanol (8–18) taken as 1.00.
§ Relative retention time for the corresponding *n*-alkyl acetate (a8–a18) taken as 1.00.
§§ Relative retention time for the compound on SE-30 taken as 1.00.

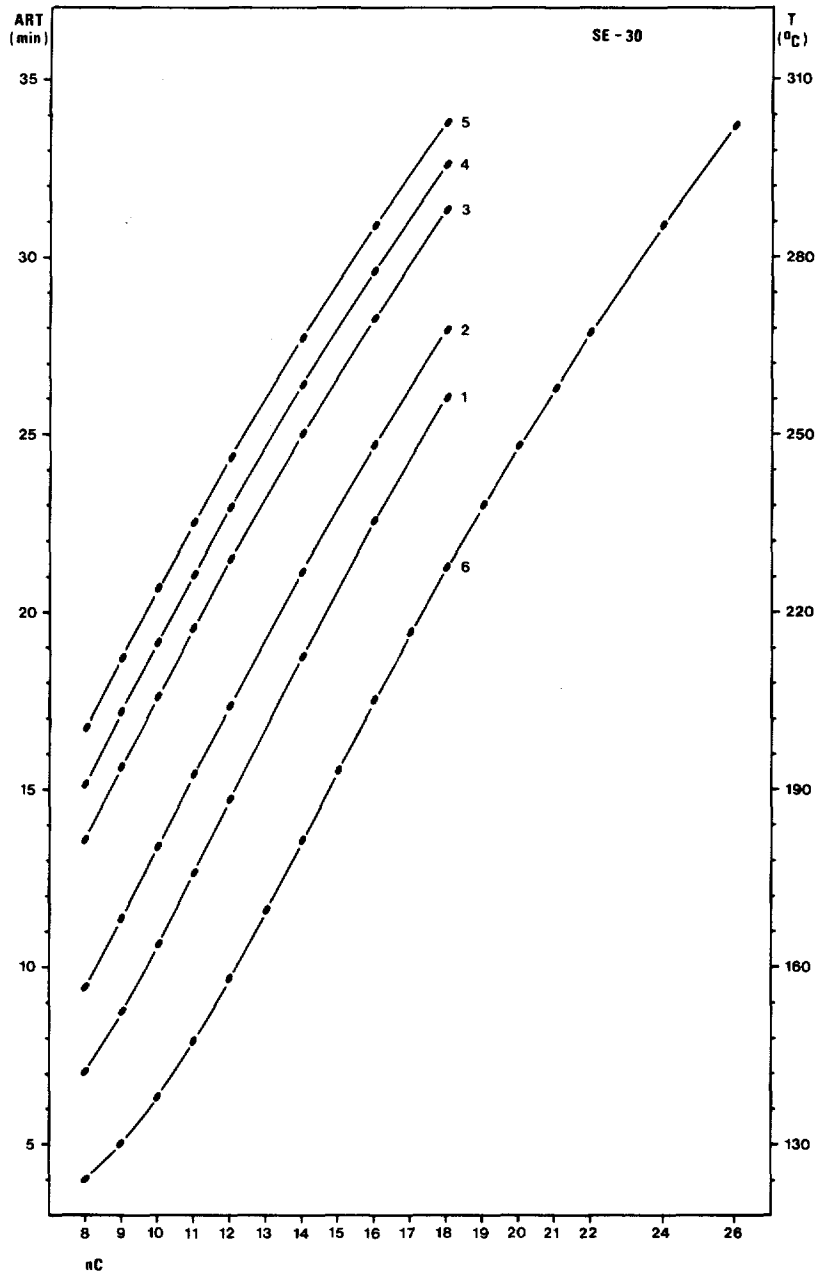

Fig. 3. Plot showing the retention of C_8–C_{18} *n*-alkanols (curve 1), *n*-alkyl acetates (curve 2), *n*-alkyl monochloroacetates (curve 3), *n*-alkyl dichloroacetates (curve 4), *n*-alkyl trichloroacetates (curve 5) and C_8–C_{26} *n*-alkanes (curve 6), obtained on SE-30 with temperature programming. ART = Absolute retention times, measured from sample injection; T = temperature of elution; *n*C = carbon number of the chain.

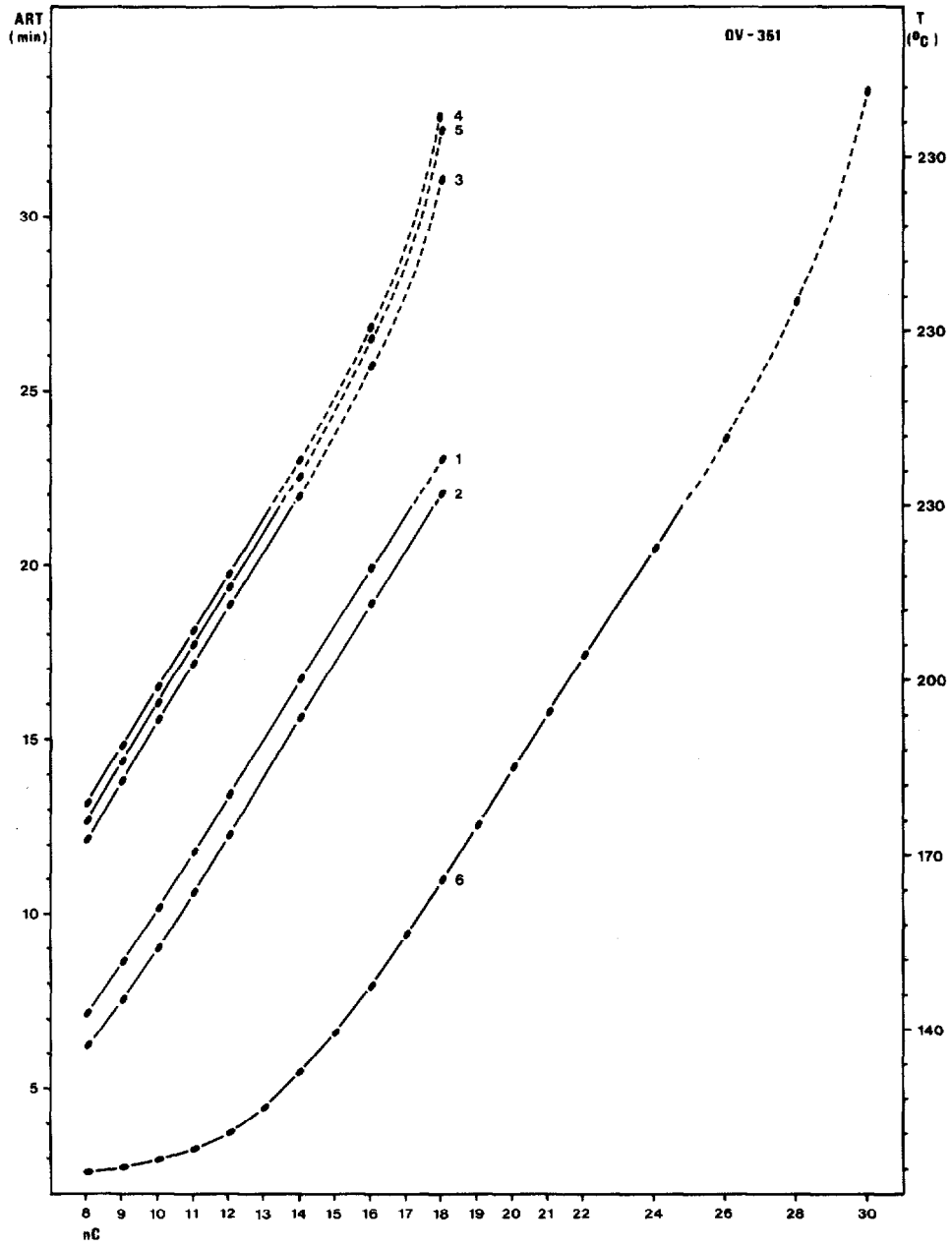

Fig. 4. Plot showing the retention of the same five series (curves 1–5) as in Fig. 3 and C_8–C_{30} *n*-alkanes (curve 6), analysed on OV-351 with temperature programming. Broken lines: isothermal conditions after reaching the final temperature.

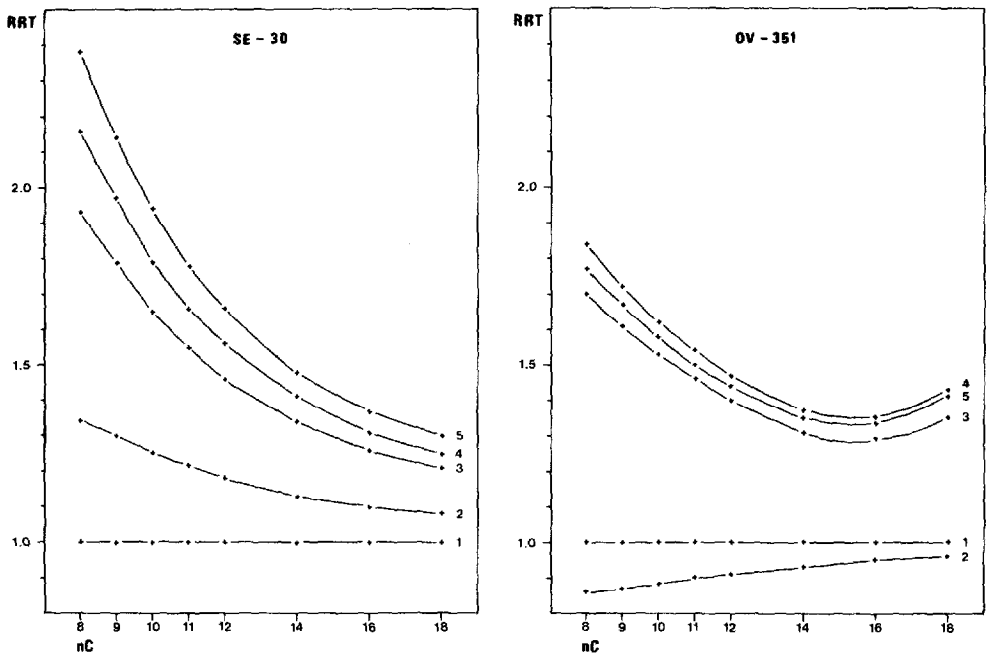

Fig. 5. Plot showing the retention of the five series (curves 1–5) as in Figs. 3 and 4, analysed on SE-30 and OV-351 using temperature programming. Relative retention time for the corresponding alkanol taken as 1.00 (Table I).

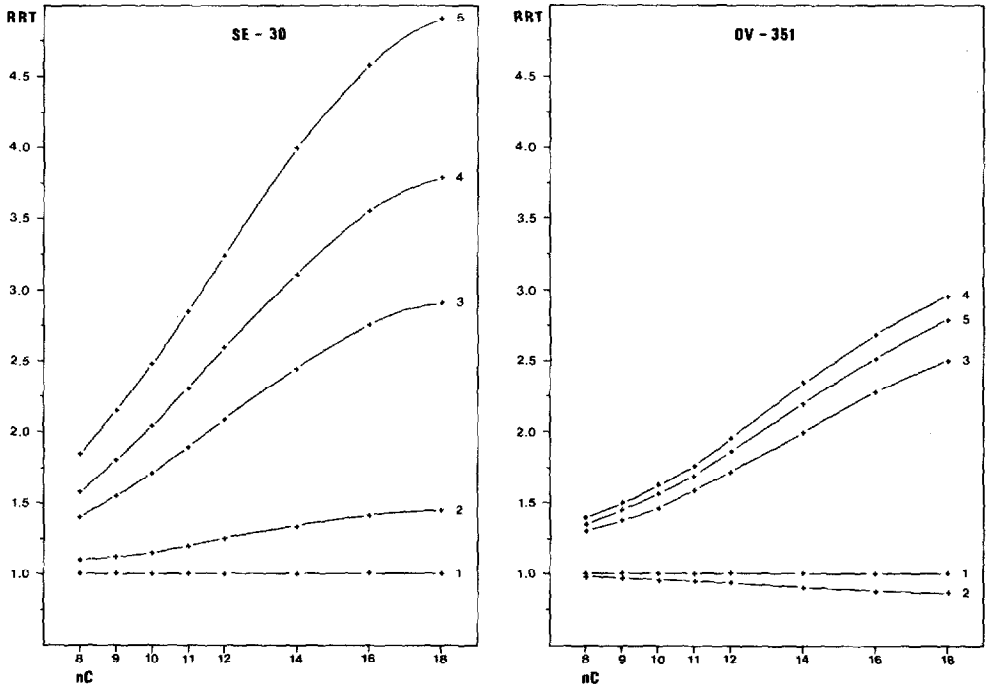

Fig. 6. Plot showing retention as in Fig. 5, determined at 200°C (Table II).

series of the lower C_1–C_8 esters on the same non-polar and polar capillary columns have been thoroughly discussed by Haken *et al.*[2] and it is certain that the same trends are also evident with the higher homologues separated in this work.

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