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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XVI*. DETERMINATION OF MONOCHLORINATED PRODUCTS FORMED IN LIQUID-PHASE CHLORINATION OF C_9–C_{12}, C_{14}, C_{16} AND C_{18} *n*-ALKYL ACETATES ON SE-30 AND OV-351 QUARTZ CAPILLARY COLUMNS WITH TEMPERATURE PROGRAMMING

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SUMMARY

Aliphatic C_9–C_{18} *n*-alkyl acetates were chlorinated with chlorine in the liquid phase in order to obtain monochlorinated products. The products were determined by gas chromatography using non-polar (SE-30) and polar (OV-351) capillary columns. All of the chloro isomers of C_9–C_{11} homologues are resolvable on OV-351; for longer chain lengths (C_{12}–C_{18}), the peaks of the mid-chain isomers from the 6-chloro to the (ω − 5)-chloro isomer overlap. On SE-30, additional overlappings of the (ω − 1)- and (ω − 2)-chloro isomers of all esters are detected, however. The retention behaviour of a mixture of all 97 components on polar and non-polar stationary phases was studied and the retention order is discussed. The SE-30 column separated the mixture better, the parent esters and their 1-chloro and ω-chloro isomers showing the greatest difference in the retention order between the columns used.

INTRODUCTION

The chlorination of C_2–C_8 *n*-alkyl acetates, chloroacetates, dichloroacetates and trichloroacetates has recently been reported[1,2]. The gas chromatographic (GC) retention behaviour of these chlorinated short-chain esters has been discussed in earlier parts of this series[3,4].

This paper describes a GC study of homologous series of aliphatic *n*-alkyl acetates (CH_3COOR), where the carbon number of the alcohol chain (R) varied between 9 and 18. The separation of a mixture of the parent esters and their isomeric monochlorinated derivatives was performed on an SE-30 and an OV-351 quartz capillary column with temperature programming. The retention data for all 97 components are tabulated relative to the parent esters and relative to *n*-tetradecane. The

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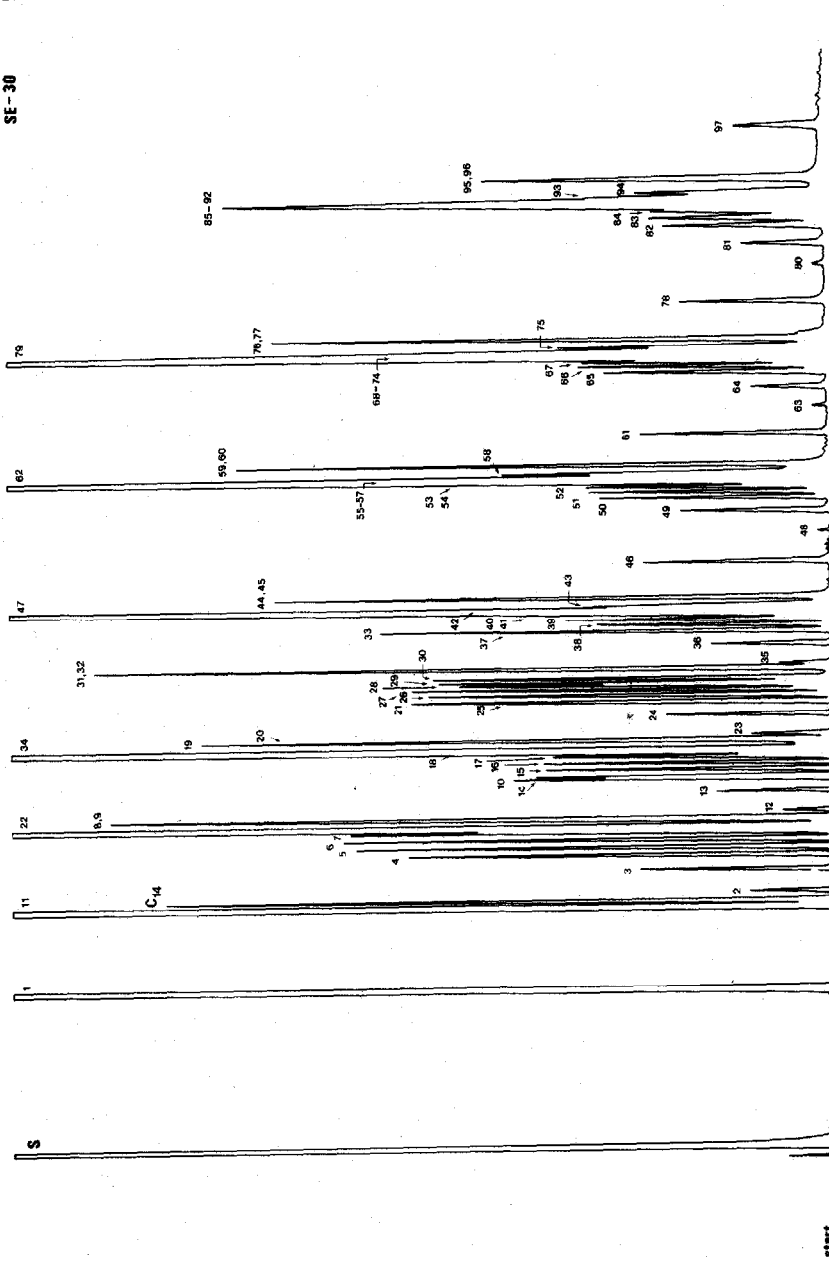

Fig. 1. Chromatogram of the mixture of aliphatic C_9–C_{18} *n*-alkyl acetates and their monochlorinated derivatives obtained on an SE-30 quartz capillary column. S = solvent; C_{14} = *n*-tetradecane; peaks are identified in Table I.

retention order of the derivatives is discussed and the isomer distributions, formed in the liquid-phase chlorinations, based on GC analyses are given.

EXPERIMENTAL

Samples

C_9–C_{12}, C_{14}, C_{16} and C_{18} *n*-alkyl acetates were prepared from commercial alcohols (Fluka, Buchs, Switzerland) and acetyl chloride (Fluka) as described earlier[5]. The monochlorinated alkyl acetates were obtained by chlorination of the corresponding parent esters with chlorine in the liquid phase at room temperature[6]. After removal of excess of the chlorination reagent and the liberated hydrogen chloride, the crude reaction mixtures were analysed by GC. The amounts of the higher chlorinated derivatives varied between 3 and 5% of the amounts of monochloro derivatives.

Apparatus

GC analyses were performed with a Perkin-Elmer Sigma 3 gas chromatograph under the following operating conditions: injector and detector (flame-ionization) temperatures, 275°C; carrier gas (nitrogen) flow-rate, 1 ml min^{-1}; splitting ratio, 1:50; and chart speed, 10 mm min^{-1}. The following columns were used: 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 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The column temperature was programmed from 50°C at 6°C min^{-1} and held at the final temperature of 260°C (SE-30) and 230°C (OV-351) 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

Gas chromatography

The isomeric monochlorinated *n*-alkyl acetates are eluted in direct order from the 1-chloro to the ω-chloro isomer both on polar and non-polar stationary phases[3]. As previously shown with short-chain (C_1–C_8) *n*-chloroalkyl acetates, the complete separation of the isomeric esters could be achieved on polar columns, whereas on SE-30 the peaks of 6-chlorooctyl and 7-chlorooctyl acetate partly overlapped[3,4].

The present results show that all of the isomeric C_9, C_{10} and C_{11} monochlorinated esters are resolvable on OV-351 and with increasing the chain length (C_{12}–C_{18}) the peaks of the mid-chain isomers from the 6-chloro to the (ω − 5)-chloro isomer always overlap. The same phenomenon has been found previously with methyl and chloromethyl monochloro esters of aliphatic C_{12}–C_{18} *n*-carboxylic acids, analysed on polar columns[7,8]. On SE-30, however, complete separation of the isomers could not be achieved, as expected, judging from the results of the incomplete resolution of *n*-chlorooctyl acetates[3,4]. With the C_9–C_{11} esters, the (ω − 1)- and (ω − 2)-chloro isomers are the only isomers that overlapped, poor separation of 6- and (ω − 5)-chloroundecanoates also being detected. The mid-chain isomers of the C_{12}–C_{18} esters overlapped, as they do on OV-351.

The gas chromatograms of the mixture of C_9–C_{18} *n*-alkyl acetates and their

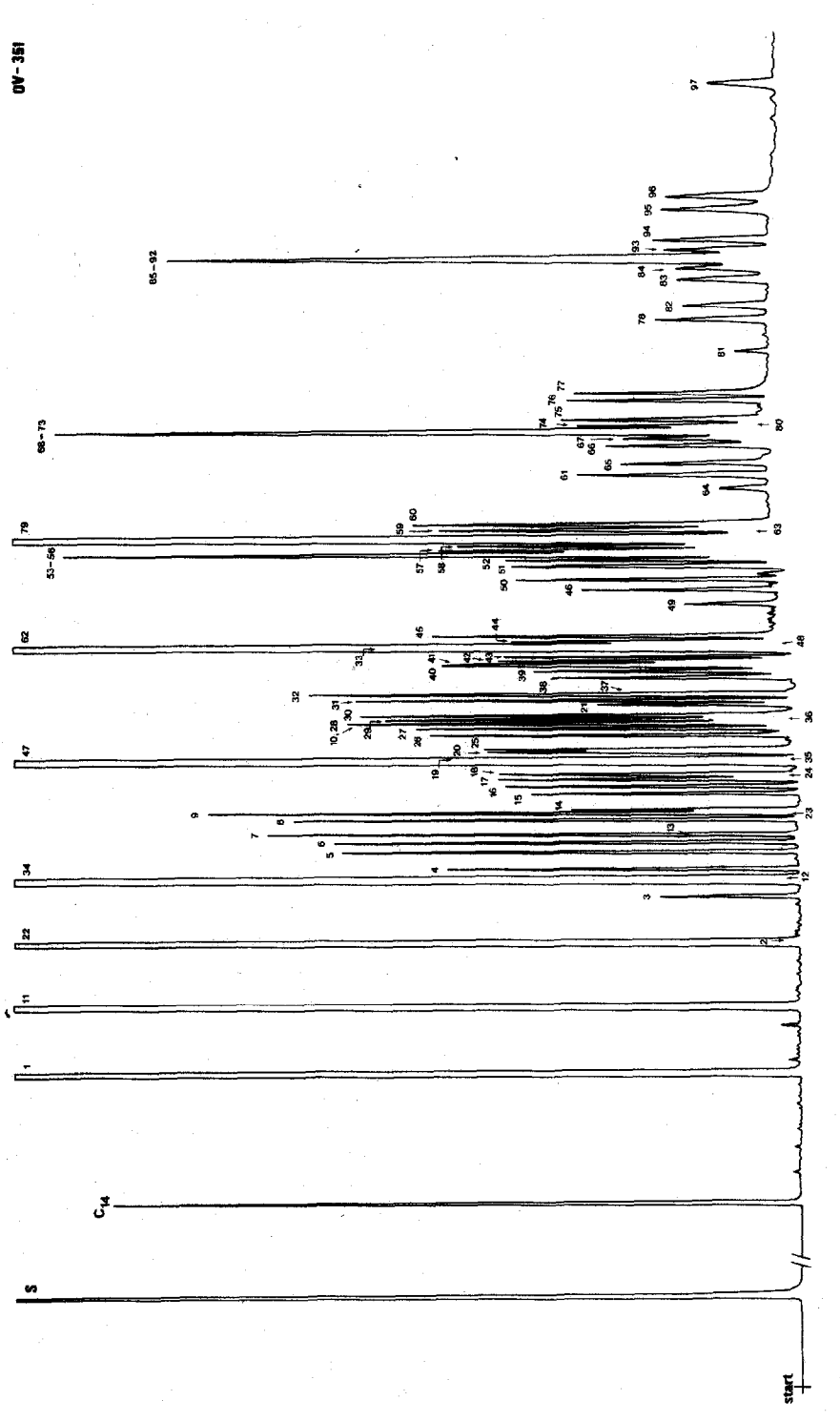

Fig. 2. Chromatogram of the mixture of aliphatic C_9–C_{18} *n*-alkyl acetates and their monochlorinated derivatives obtained on an OV-351 quartz capillary column. S = solvent; C_{14} = *n*-tetradecane; peaks are identified in Table I.

monochlorinated derivatives with *n*-tetradecane obtained on SE-30 and OV-351 are illustrated in Figs. 1 and 2, respectively. The retention data of the compounds are given in Table I. As shown, a non-polar column separated the mixture of all 97 components better than a polar column, although some overlappings occurred in addition to those mentioned above. Fig. 1 shows that C_n parent esters ($n \geqslant 11$) always overlap with the mid-chain chloro isomers of the C_{n-2} ester, whereas on OV-351 the overlappings with the parent esters are negligible, owing to their earlier elution compared with chlorinated isomers (Fig. 2). Only two additional overlappings between the chloro esters on SE-30 are found, *i.e.*, 10-chlorodecyl acetate (21) with 3-chloroundecyl acetate (25) and 11-chloroundecyl acetate (33) with 3-chlorododecyl acetate (37). The several overlappings that occurred on OV-351 are illustrated in Fig. 2, showing, *e.g.*, that none of the 1-chloro isomers is resolved.

Table II gives the elution order of the compounds. As shown, the parent esters and their 1-chloro and ω-chloro derivatives give rise to the greatest difference in elution orders between the columns used. The parent esters have relatively high retention times on SE-30 and their monochlorinated isomers are eluted close together, *e.g.*, all C_{14} isomers before the C_{16} isomers and all C_{16} isomers before the C_{18} isomers, as shown in Fig. 1. On OV-351, however, the 1-chloro isomers are eluted relatively early, whereas for the ω-chloro isomers relatively long retention times are observed *e.g.*, 1-chlorotetradecyl acetate (48) eluted before 10-chlorododecyl acetate (44) and 14-chlorotetradecyl acetate (61) after 2-chlorohexadecyl acetate (64) (Fig. 2 and Table II).

The last column in Table I shows that longer retention times of compounds on SE-30 are found, except for compounds 10 and 97, 18-chlorooctadecyl acetate (97) being eluted earlier on SE-30 owing to the higher final temperature used. As previously reported, longer retention times of C_1–C_8 *n*-alkyl acetates on OV-351 are always detected[4].

TABLE I

ABSOLUTE (ART) AND RELATIVE RETENTION TIMES (RRT) OF ALIPHATIC C_9–C_{18} *n*-ALKYL ACETATES AND THEIR MONOCHLORINATED DERIVATIVES ON SE-30 AND OV-351 QUARTZ CAPILLARY COLUMNS

Conditions as shown in Figs. 1 and 2.

Peak No.	*n-Alkyl acetate: R in CH_3COOR*	*Column*						
		SE-30			*OV-351*			
		*ART**	*RRT***	*RRT****	*ART**	*RRT***	*RRT****	*RRT§*
1	Nonyl	19.10	1.00	0.88	14.90	1.00	1.34	0.78
2	1-Chlorononyl	21.86	1.14	1.01	18.71	1.26	1.68	0.86
3	2-Chlorononyl	22.43	1.17	1.04	20.01	1.34	1.80	0.89
4	3-Chlorononyl	22.85	1.20	1.06	20.81	1.40	1.87	0.91
5	4-Chlorononyl	23.09	1.21	1.07	21.30	1.43	1.92	0.92
6	5-Chlorononyl	23.29	1.22	1.08	21.58	1.45	1.94	0.93
7	6-Chlorononyl	23.50	1.23	1.09	21.81	1.46	1.96	0.93
8	7-Chlorononyl	23.83	1.25	1.10	22.28	1.50	2.01	0.93
9	8-Chlorononyl	23.87	1.25	1.11	22.43	1.51	2.02	0.93
10	9-Chlorononyl	24.95	1.31	1.16	25.06	1.68	2.26	1.00

(Continued on p. 24)

TABLE I *(continued)*

Peak No.	*n-Alkyl acetate: R in CH_3COOR*	*Column*						
		SE-30			*OV-351*			
		*ART**	*RRT***	*RRT****	*ART**	*RRT***	*RRT****	*RRT§*
11	Decyl	21.40	1.00	0.99	16.80	1.00	1.51	0.79
12	1-Chlorodecyl	24.04	1.12	1.11	20.50	1.22	1.85	0.85
13	2-Chlorodecyl	24.60	1.15	1.14	21.75	1.29	1.96	0.88
14	3-Chlorodecyl	25.01	1.17	1.16	22.51	1.34	2.03	0.90
15	4-Chlorodecyl	25.21	1.18	1.17	23.00	1.37	2.07	0.91
16	5-Chlorodecyl	25.40	1.19	1.18	23.21	1.38	2.09	0.91
17	6-Chlorodecyl	25.58	1.20	1.18	23.42	1.39	2.11	0.92
18	7-Chlorodecyl	25.70	1.20	1.19	23.59	1.40	2.12	0.92
19	8-Chlorodecyl	26.00	1.21	1.20	24.00	1.43	2.16	0.92
20	9-Chlorodecyl	26.02	1.22	1.21	24.21	1.44	2.18	0.93
21	10-Chlorodecyl	27.07	1.26	1.25	25.59	1.52	2.30	0.95
22	Undecyl	23.61	1.00	1.09	18.69	1.00	1.68	0.79
23	1-Chloroundecyl	26.18	1.11	1.21	22.30	1.19	2.01	0.85
24	2-Chloroundecyl	26.71	1.13	1.24	23.50	1.26	2.12	0.88
25	3-Chloroundecyl	27.07	1.15	1.25	24.29	1.30	2.19	0.90
26	4-Chloroundecyl	27.29	1.16	1.26	24.71	1.32	2.22	0.91
27	5-Chloroundecyl	27.42	1.16	1.27	24.90	1.33	2.24	0.91
28	6-Chloroundecyl	27.56	1.17	1.28	25.06	1.34	2.26	0.91
29	7-Chloroundecyl	27.62	1.17	1.28	25.17	1.35	2.27	0.91
30	8-Chloroundecyl	27.73	1.17	1.28	25.29	1.35	2.28	0.91
31	9-Chloroundecyl	27.98	1.19	1.30	25.71	1.38	2.31	0.92
32	10-Chloroundecyl	28.00	1.19	1.30	25.90	1.39	2.33	0.93
33	11-Chloroundecyl	29.02	1.23	1.34	27.21	1.46	2.45	0.94
34	Dodecyl	25.72	1.00	1.19	20.50	1.00	1.86	0.80
35	1-Chlorododecyl	28.11	1.09	1.30	23.91	1.16	2.15	0.85
36	2-Chlorododecyl	28.65	1.11	1.33	25.15	1.23	2.26	0.88
37	3-Chlorododecyl	29.02	1.13	1.34	25.90	1.26	2.33	0.89
38	4-Chlorododecyl	29.20	1.14	1.35	26.35	1.29	2.37	0.90
39	5-Chlorododecyl	29.35	1.14	1.36	26.53	1.29	2.39	0.90
40	6-Chlorododecyl	29.49	1.15	1.37	26.70	1.30	2.40	0.91
41	7-Chlorododecyl	29.51	1.15	1.37	26.72	1.30	2.41	0.91
42	8-Chlorododecyl	29.62	1.15	1.37	26.82	1.31	2.41	0.91
43	9-Chlorododecyl	29.71	1.16	1.38	26.95	1.31	2.43	0.91
44	10-Chlorododecyl	29.98	1.17	1.39	27.40	1.34	2.47	0.91
45	11-Chlorododecyl	29.98	1.17	1.39	27.58	1.35	2.48	0.92
46	12-Chlorododecyl	30.91	1.20	1.43	28.89	1.41	2.60	0.93
47	Tetradecyl	29.60	1.00	1.37	23.96	1.00	2.16	0.81
48	1-Chlorotetradecyl	31.81	1.07	1.47	27.28	1.14	2.46	0.86
49	2-Chlorotetradecyl	32.33	1.09	1.50	28.46	1.19	2.56	0.88
50	3-Chlorotetradecyl	32.69	1.10	1.51	29.20	1.22	2.63	0.89
51	4-Chlorotetradecyl	32.86	1.11	1.52	29.60	1.24	2.66	0.90
52	5-Chlorotetradecyl	32.99	1.11	1.53	29.79	1.24	2.68	0.90
53	6-Chlorotetradecyl	33.10	1.12	1.53	29.93	1.25	2.69	0.90
54	7-Chlorotetradecyl	33.10	1.12	1.53	29.93	1.25	2.69	0.90
55	8-Chlorotetradecyl	33.19	1.12	1.54	29.97	1.25	2.70	0.90

TABLE I *(continued)*

Peak No.	*n-Alkyl acetate: R in CH_3COOR*	*Column*						
		SE-30			*OV-351*			
		*ART**	*RRT***	*RRT****	*ART**	*RRT***	*RRT****	*RRT§*
56	9-Chlorotetradecyl	33.23	1.12	1.54	30.00	1.25	2.70	0.90
57	10-Chlorotetradecyl	33.29	1.12	1.54	30.09	1.26	2.71	0.90
58	11-Chlorotetradecyl	33.39	1.13	1.55	30.20	1.26	2.72	0.90
59	12-Chlorotetradecyl	33.60	1.14	1.56	30.65	1.28	2.76	0.91
60	13-Chlorotetradecyl	33.60	1.14	1.56	30.81	1.29	2.77	0.92
61	14-Chlorotetradecyl	34.48	1.16	1.60	32.28	1.35	2.91	0.94
62	Hexadecyl	33.20	1.00	1.54	27.27	1.00	2.45	0.82
63	1-Chlorohexadecyl	35.26	1.06	1.63	30.56	1.12	2.75	0.87
64	2-Chlorohexadecyl	35.79	1.08	1.66	31.85	1.17	2.87	0.89
65	3-Chlorohexadecyl	36.15	1.09	1.67	32.60	1.20	2.93	0.90
66	4-Chlorohexadecyl	36.31	1.09	1.68	33.10	1.21	2.98	0.91
67	5-Chlorohexadecyl	36.44	1.10	1.69	33.31	1.22	3.00	0.91
68	6-Chlorohexadecyl	36.59	1.10	1.69	33.50	1.23	3.02	0.92
69	7-Chlorohexadecyl	36.59	1.10	1.69	33.50	1.23	3.02	0.92
70	8-Chlorohexadecyl	36.62	1.10	1.70	33.54	1.23	3.02	0.92
71	9-Chlorohexadecyl	36.62	1.10	1.70	33.54	1.23	3.02	0.92
72	10-Chlorohexadecyl	36.64	1.10	1.70	33.56	1.23	3.02	0.92
73	11-Chlorohexadecyl	36.68	1.10	1.70	33.58	1.23	3.02	0.92
74	12-Chlorohexadecyl	36.79	1.11	1.70	33.69	1.24	3.03	0.92
75	13-Chlorohexadecyl	36.86	1.11	1.71	33.85	1.24	3.05	0.92
76	14-Chlorohexadecyl	37.09	1.12	1.72	34.41	1.26	3.10	0.93
77	15-Chlorohexadecyl	37.09	1.12	1.72	34.65	1.27	3.12	0.93
78	16-Chlorohexadecyl	38.11	1.15	1.77	36.75	1.35	3.31	0.96
79	Octadecyl	36.60	1.00	1.70	30.40	1.00	2.73	0.83
80	1-Chlorooctadecyl	39.10	1.07	1.81	33.61	1.11	3.03	0.86
81	2-Chlorooctadecyl	39.71	1.08	1.84	35.82	1.18	3.22	0.90
82	3-Chlorooctadecyl	40.20	1.10	1.86	37.15	1.22	3.34	0.92
83	4-Chlorooctadecyl	40.41	1.10	1.87	37.91	1.25	3.41	0.93
84	5-Chlorooctadecyl	40.61	1.11	1.88	38.23	1.26	3.44	0.94
85	6-Chlorooctadecyl	40.73	1.11	1.89	38.45	1.26	3.46	0.94
86	7-Chlorooctadecyl	40.73	1.11	1.89	38.45	1.26	3.46	0.94
87	8-Chlorooctadecyl	40.77	1.11	1.89	38.50	1.27	3.47	0.94
88	9-Chlorooctadecyl	40.77	1.11	1.89	38.50	1.27	3.47	0.94
89	10-Chlorooctadecyl	40.80	1.11	1.89	38.53	1.27	3.47	0.94
90	11-Chlorooctadecyl	40.80	1.11	1.89	38.55	1.27	3.47	0.94
91	12-Chlorooctadecyl	40.83	1.12	1.89	38.58	1.27	3.47	0.95
92	13-Chlorooctadecyl	40.85	1.12	1.89	38.62	1.27	3.48	0.95
93	14-Chlorooctadecyl	40.96	1.12	1.90	38.79	1.28	3.49	0.95
94	15-Chlorooctadecyl	41.10	1.12	1.90	39.06	1.28	3.52	0.95
95	16-Chlorooctadecyl	41.47	1.13	1.92	39.96	1.31	3.60	0.96
96	17-Chlorooctadecyl	41.47	1.13	1.92	40.35	1.33	3.63	0.97
97	18-Chlorooctadecyl	42.96	1.17	1.99	43.59	1.43	3.92	1.01

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

** Relative retention time for the corresponding parent ester taken as 1.00.

*** Relative retention time for *n*-tetradecane (C_{14}) taken as 1.00. Absolute retention time of *n*-tetradecane: 21.59 min (SE-30) and 11.11 min (OV-351).

§ Relative retention times for compounds on SE-30 taken as 1.00.

TABLE II

ELUTION ORDER OF ALIPHATIC C_9–C_{18} *n*-ALKYL ACETATES AND THEIR MONOCHLORINATED DERIVATIVES ON SE-30 AND OV-351 QUARTZ CAPILLARY COLUMNS

Conditions as shown in Figs. 1 and 2.

Column	*Elution order of compounds**
SE-30	$^{1}_{9}$ $^{2}_{10}$ $^{3}_{9}$ $^{4}_{9}$ $^{5}_{9}$ $^{6}_{9}$ $^{7}_{11}$ $^{8}_{9}$ $^{9}_{9}$ $^{1}_{10}$ $^{2}_{10}$ $^{9}_{9}$ $^{3}_{10}$ $^{4}_{10}$ $^{5}_{10}$ $^{6}_{10}$ $^{7}_{10}$ $^{8}_{12}$ $^{9}_{10}$ $^{1}_{10}$ $^{2}_{11}$ $^{3}_{11}$ $^{10}_{11}$ $^{4}_{10}$ $^{5}_{11}$ $^{6}_{11}$ $^{7}_{11}$ $^{8}_{11}$ $^{9}_{11}$ $^{10}_{11}$ $^{1}_{12}$ $^{2}_{12}$ $^{3}_{12}$ $^{11}_{11}$ $^{4}_{12}$
OV-351	$^{1}_{9}$ $^{2}_{10}$ $^{3}_{11}$ $^{1}_{9}$ $^{2}_{9}$ $^{9}_{12}$ $^{1}_{10}$ $^{3}_{9}$ $^{4}_{9}$ $^{5}_{9}$ $^{2}_{10}$ $^{6}_{9}$ $^{7}_{9}$ $^{1}_{11}$ $^{8}_{9}$ $^{3}_{19}$ $^{4}_{10}$ $^{5}_{10}$ $^{6}_{10}$ $^{2}_{11}$ $^{7}_{10}$ $^{1}_{12}$ $^{8}_{14}$ $^{9}_{10}$ $^{3}_{10}$ $^{4}_{11}$ $^{5}_{11}$ $^{6}_{11}$ $^{9}_{11}$ $^{2}_{9}$ $^{7}_{12}$ $^{8}_{11}$ $^{10}_{11}$ $^{9}_{10}$ $^{10}_{11}$ $^{3}_{11}$ $^{4}_{12}$ $^{12}_{12}$
SE-30 (*continued*)	$^{5}_{12}$ $^{6}_{12}$ $^{7}_{12}$ $^{8}_{14}$ $^{9}_{12}$ $^{10}_{12}$ $^{11}_{12}$ $^{12}_{12}$ $^{1}_{14}$ $^{2}_{14}$ $^{3}_{14}$ $^{4}_{14}$ $^{5}_{14}$ $^{6}_{14}$ $^{7}_{14}$ $^{8}_{16}$ $^{9}_{14}$ $^{10}_{14}$ $^{11}_{14}$ $^{12}_{14}$ $^{13}_{14}$ $^{14}_{16}$ $^{1}_{16}$ $^{2}_{16}$ $^{3}_{16}$ $^{4}_{16}$ $^{5}_{16}$ $^{6}_{16}$ $^{7}_{18}$ $^{8}_{16}$ $^{9}_{16}$ $^{10}_{16}$ $^{11}_{16}$
OV-351 (*continued*)	$^{5}_{12}$ $^{6}_{12}$ $^{7}_{12}$ $^{8}_{12}$ $^{9}_{12}$ $^{11}_{11}$ $^{1}_{16}$ $^{10}_{14}$ $^{11}_{12}$ $^{2}_{12}$ $^{12}_{14}$ $^{3}_{12}$ $^{4}_{14}$ $^{5}_{14}$ $^{6}_{14}$ $^{7}_{14}$ $^{8}_{14}$ $^{9}_{14}$ $^{10}_{14}$ $^{11}_{14}$ $^{1}_{18}$ $^{12}_{16}$ $^{13}_{14}$ $^{2}_{14}$ $^{14}_{16}$ $^{3}_{14}$ $^{4}_{16}$ $^{5}_{16}$ $^{6}_{16}$ $^{7}_{16}$ $^{8}_{16}$ $^{9}_{16}$ $^{10}_{16}$ $^{11}_{16}$
SE-30 (*continued*)	$^{12}_{16}$ $^{13}_{16}$ $^{14}_{16}$ $^{15}_{16}$ $^{16}_{16}$ $^{1}_{18}$ $^{2}_{18}$ $^{3}_{18}$ $^{4}_{18}$ $^{5}_{18}$ $^{6}_{18}$ $^{7}_{18}$ $^{8}_{18}$ $^{9}_{18}$ $^{10}_{18}$ $^{11}_{18}$ $^{12}_{18}$ $^{13}_{18}$ $^{14}_{18}$ $^{15}_{18}$ $^{16}_{18}$ $^{17}_{18}$ $^{18}_{18}$
OV-351 (*continued*)	$^{1}_{18}$ $^{12}_{16}$ $^{13}_{16}$ $^{14}_{16}$ $^{15}_{16}$ $^{2}_{18}$ $^{16}_{16}$ $^{3}_{18}$ $^{4}_{18}$ $^{5}_{18}$ $^{6}_{18}$ $^{7}_{18}$ $^{8}_{18}$ $^{9}_{18}$ $^{10}_{18}$ $^{11}_{18}$ $^{12}_{18}$ $^{13}_{18}$ $^{14}_{18}$ $^{15}_{18}$ $^{16}_{18}$ $^{17}_{18}$ $^{18}_{18}$

* Notation of compounds: 9–18 are the parent esters from nonyl acetate (9) to octadecyl acetate (18); the upper number indicates the position of the Cl substituent, the lower number the alcohol chain length (*e.g.*, $^{8}_{9}$ denotes 8-chlorononyl acetate).

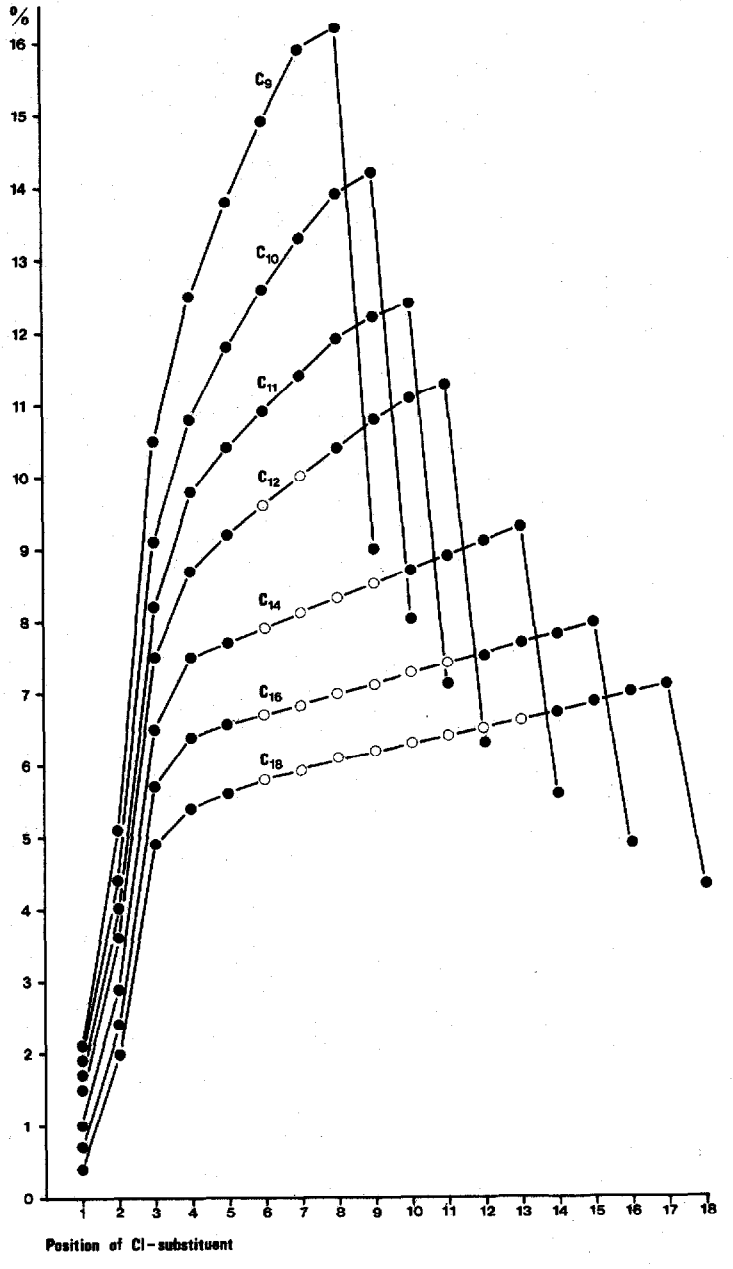

Fig. 3. Isomer distribution of monochlorinated C_9–C_{18} *n*-alkyl acetates based on GC analyses on an OV-351 quartz capillary column. ●, Observed values; ○, estimated values; averages of two independent chlorination processes, agreeing to within ±3%.

Isomer distribution

Fig. 3 illustrates the isomer distribution of the monochlorinated products based on GC analyses on OV-351. Owing to the overlapping, the amounts of the mid-chain isomers of the C_{12}–C_{18} esters are estimates[9,10]. The amounts of the isomers are assumed to increase with increasing distance between the chloro and the ester groups, as in the case of the resolved (C_9–C_{11}) isomers. In the absence of model samples, the isomer distributions are determined without weight response correction factors[11]. It seems evident, however, that the true proportions of the 1-chloroalkyl esters, owing to their instability[1], are greater than those presented. Table III gives the relative amounts of products, tabulated relative to the ω-chloro isomers (= 100). The results are in good agreement with those of the lower homologues reported earlier[1,2], the main products always being the (ω − 1)-chloro isomers. Table III shows that the relative amounts of the 1-chloro isomers remain unchanged in C_9–C_{12} esters, but decrease with increasing chain length. The small amount of 1-chlorooctadecyl acetate found indicates its lower stability compared with the other isomers. Additional evidence of the instability of the long-chain chloro isomers could be observed using isothermal operating conditions at high temperatures (220–260°C). The response of the isomers decreased strongly and new peaks were detected in the chromatograms just after the peak of the parent ester. These new compounds are evidently unsaturated *n*-alkyl acetates, formed by the dehydrochlorination of the chloroalkyl

TABLE III

RELATIVE AMOUNTS* OF MONOCHLORINATED ISOMERS FORMED IN THE CHLORINATION OF ALIPHATIC C_9–C_{18} *n*-ALKYL ACETATES

Isomeric monochloro ester	*n-Alkyl acetate, chain length*						
	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{16}	C_{18}
1-Cl	24	24	24	24	18	14	9
2-Cl	57	55	56	57	52	49	47
3-Cl	117	114	115	119	116	116	114
4-Cl	139	135	138	138	134	131	126
5-Cl	153	148	146	146	138	135	130
6-Cl	166	158	154	152	141	137	135
7-Cl	177	166	161	159	145	139	137
8-Cl	180	174	168	165	148	143	142
9-Cl	100	178	172	171	152	145	144
10-Cl		100	175	176	155	149	147
11-Cl			100	179	159	151	149
12-Cl				100	163	153	151
13-Cl					166	157	153
14-Cl					100	159	156
15-Cl						163	158
16-Cl						100	163
17-Cl							165
18-Cl							100

* Relative to the ω-chloro isomers (= 100); the values are averages of two independent experiments and agree to within ±3%. Values for the 6-chloro to the (ω − 5)-chloro isomers of C_{12}–C_{18} esters are estimates.

acetates during GC analysis at high temperature. Owing to the dehydrochlorination the peaks of some 1-chloroalkyl acetates are not detected.

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