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GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XVII*. SEPARATION OF A MIXTURE OF PRIMARY C_1–C_{18} STRAIGHT-CHAIN ALCOHOLS AND THEIR PROPANOYL, 2-CHLOROPROPANOYL AND 3-CHLOROPROPANOYL DERIVATIVES ON SE-30 AND OV-351 CAPILLARY COLUMNS WITH TEMPERATURE PROGRAMMING

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SUMMARY

Primary straight-chain C_1–C_{12}, C_{14}, C_{16} and C_{18} alcohols and their propanoyl, 2-chloropropanoyl and 3-chloropropanoyl derivatives have been analysed by gas chromatography on SE-30 and OV-351 capillary columns. The separation of a mixture of 60 components was complete on SE-30, some overlapping occurring on OV-351. As expected, the retention times of the homologous series increase with increasing chain length. The order of elution of the individual components in the mixture from SE-30 was C_{n+2}-alcohol < C_n-alkyl propanoate < C_{n-2}-alkyl 3-chloropropanoate < C_{n-1}-alkyl 2-chloropropanoate. The corresponding order on OV-351, C_n-alkyl propanoate < C_n-alcohol < C_{n-4}-alkyl 3-chloropropanoate < C_{n-2}-alkyl 2-chloropropanoate ($n \geqslant 6$), indicates the relatively shorter retention times of *n*-alkyl propanoates and relatively higher retention times of their monochlorinated derivatives. The short-chain (C_1–C_4) alcohols are eluted earlier than the corresponding *n*-alkyl propanoates on the polar column. The retention data for all compounds are given.

INTRODUCTION

The gas chromatographic (GC) retention behaviour of homologous esters has been extensively studied, *e.g.*, by Haken and co-workers[1,2]. The interest in halogenated carboxylic acid derivatives has increased owing to their important biochemical properties, *e.g.*, as herbicides and bacteriocides. Previously, a series of studies designed to maximize the separation of complex mixtures of various chlorinated esters with substitution in both the acyl and alkyl chains were reported[3–9], using temperature programming and non-polar and polar capillary columns. Capillary column chromatography of alkyl acetates, chloroacetates, dichloroacetates and trichloroacetates

* For Part XVI, see ref. 6.

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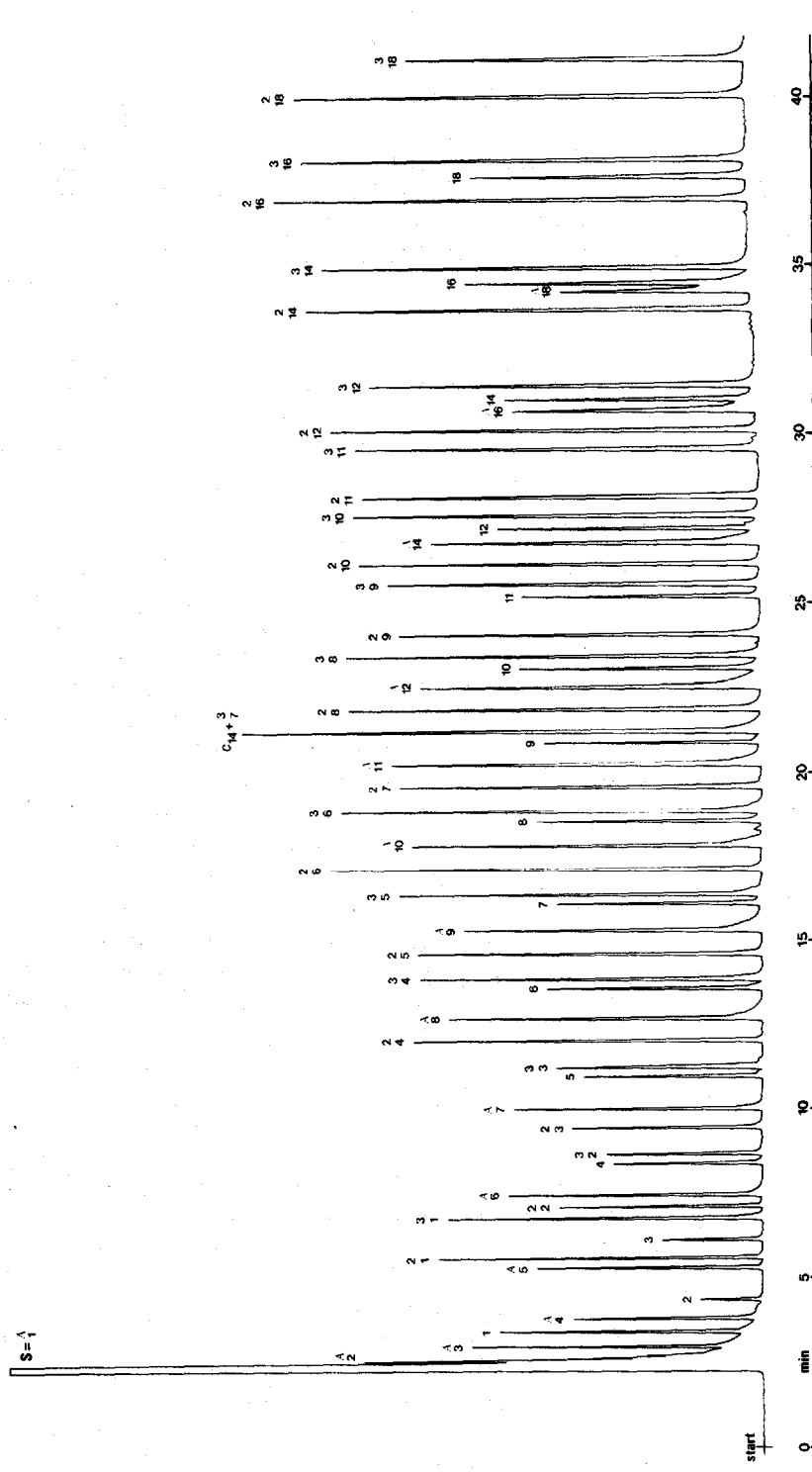

Fig. 1. Chromatogram of a mixture of primary C_1–C_{18} straight-chain alcohols ($\overset{A}{1}$–$\overset{A}{18}$) and the corresponding *n*-alkyl propanoates (1–18), *n*-alkyl 2-chloropropanoates ($\overset{2}{1}$–$\overset{2}{18}$) and *n*-alkyl 3-chloropropanoates ($\overset{3}{1}$–$\overset{3}{18}$), analysed on SE-30. Methanol ($\overset{\wedge}{1}$) = solvent; C_{14} = *n*-tetradecane. The upper number indicates the position of the Cl substituent, the lower number the chain length.

and of chlorinated phenyl acetates was carried out to elucidate the effect of structure on retention increments[10,11]. Komárek *et al.*[12,13] studied the GC of homologous series of halogenated esters containing fluorine, chlorine, bromine and iodine in either the alcohol or the acid moiety of the ester on packed and capillary columns with several stationary phases. The GC of alcohols has been widely studied, *e.g.*, by Castello and co-workers[14,15], and the GC behaviour of long-chain alcohols and their derivatives was described, *e.g.*, by VandenHeuvel *et al.*[16].

The present paper describes the GC of primary straight-chain C_1–C_{12}, C_{14}, C_{16} and C_{18} alcohols, particularly their propanoyl, 2-chloropropanoyl and 3-chloropropanoyl derivatives. The separation of a mixture of 60 components was carried out on SE-30 and OV-351 quartz capillary columns with temperature programming. The relative retention times for all compounds are given and the retention behaviour on non-polar and polar stationary phases is discussed.

EXPERIMENTAL

Materials

The C_1–C_{12}, C_{14}, C_{16} and C_{18} alcohols were commercial products (Fluka, Buchs, Switzerland). *n*-Alkyl propanoates, 2-chloropropanoates and 3-chloropropanoates were prepared from the corresponding alcohols and acid chlorides as described earlier[17]; propanoyl chloride was obtained by the reaction of benzoyl chloride (Fluka) with propanoic acid (Fluka) according to Brown[18], 2-chloropropanoyl chloride by chlorination[19] of propanoyl chloride with N-chlorosuccinimide (E. Merck, Darmstadt, F.R.G.) and 3-chloropropanoyl chloride from 3-chloropropanoic acid[20] by treatment with thionyl chloride. The purity of the compounds was checked by GC, the retention time of the homologues increasing with increase in the alkyl chain length.

Methods

The GC analyses were carried out by use of a Perkin-Elmer Sigma 3 gas chromatograph under the following operating conditions: injector and flame ionization detector temperatures, 275°C; nitrogen carrier gas flow-rate, 1 ml min^{-1}; splitting ratio, 1:50; 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 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The following column temperatures were used: SE-30, programmed from 50 to 300°C at 6°C min^{-1}; OV-351, programmed from 50 to 230°C at 6°C min^{-1} and maintained at 230°C until the elution of peaks had ceased.

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

RESULTS AND DISCUSSION

Figs. 1 and 2 show the separations of the C_1–C_{18} free alcohols and the corresponding *n*-alkyl propanoates, 2-chloropropanoates and 3-chloropropanoates on SE-30 and OV-351 capillary columns. Table I gives the absolute and the relative

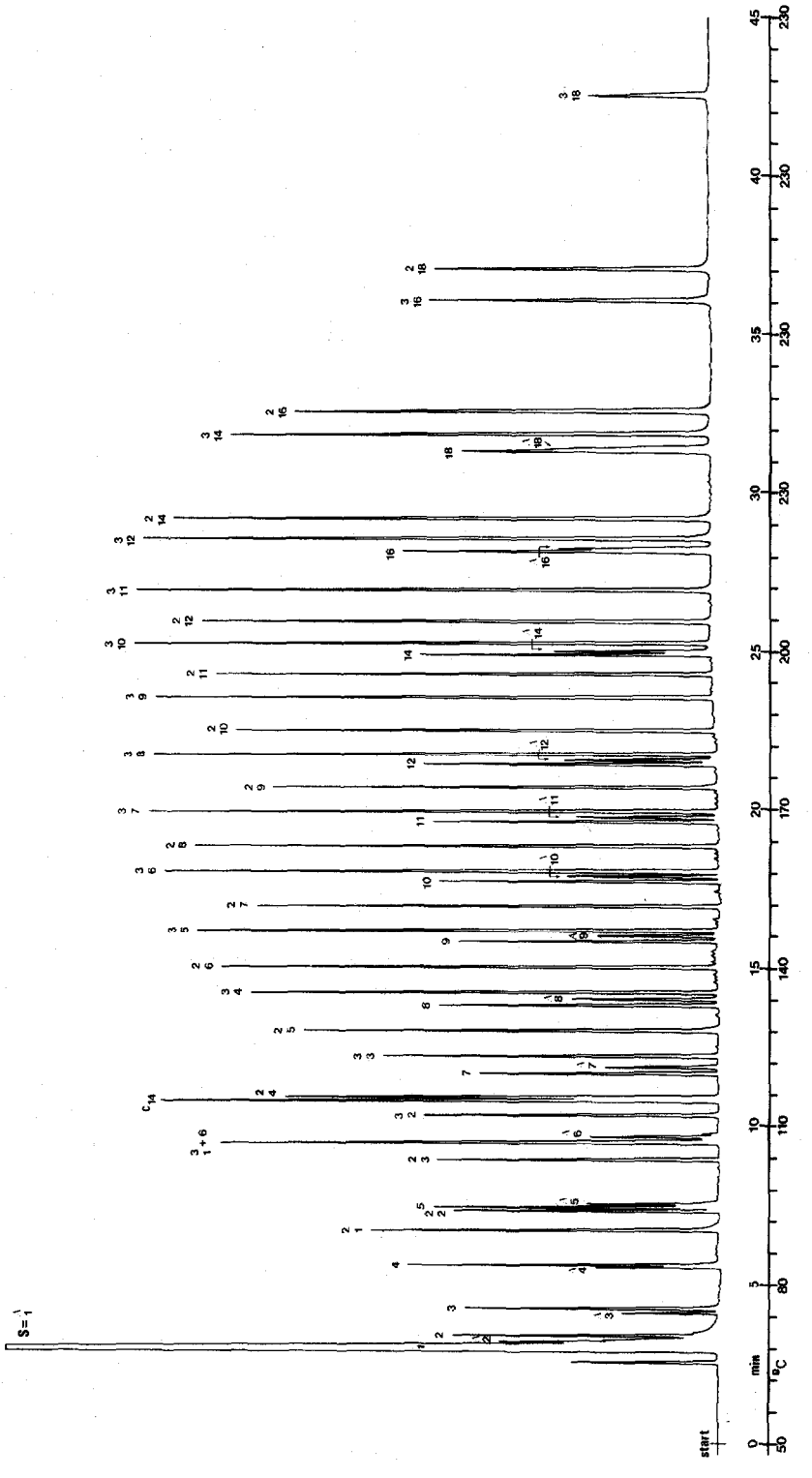

Fig. 2. Chromatogram of the same mixture as in Fig. 1, analysed on OV-351.

retention times of the compounds, relative to *n*-alcohols, *n*-alkyl propanoates and *n*-tetradecane. The retentions are also expressed as the ratios of the retention times of the compounds on OV-351 to those on SE-30.

As expected, the retention times of the compounds in the four homologous series increase with the length of the chain. Fig. 1 shows that a non-polar SE-30 column gave a complete separation of the mixture, *n*-tetradecane being eluted at nearly the same time as heptyl 3-chloropropanoate (Table I). However, SE-30 seems to be somewhat unsuitable for alcohols, giving tailing peaks, particularly for the long-chain isomers. All derivatives are eluted later than the parent alcohols, in the following order (Fig. 1): C_{n+2}-alcohol < C_n-alkyl propanoate < C_{n-2}-alkyl 3-chloropropanoate < C_{n-1}-alkyl 2-chloropropanoate. The only exception on SE-30 constitutes the pair 1-pentanol and methyl 2-chloropropanoate, eluted in that order. Three lower alcohols are eluted before methyl propanoate and five lower alcohols earlier than monochlorinated methyl propanoates (Fig. 1).

The use of a highly polar OV-351 capillary column led to poorer separation of the mixture, as shown in Fig. 2, *i.e.*, methyl propanoate overlapped with solvent (methanol) and hexyl propanoate and methyl 3-chloropropanoate were coincident. In addition, the peaks of the C_4, C_5, C_{14}, C_{16} and C_{18} alcohols and the corresponding *n*-alkyl propanoates are poorly separated. Generally, the following elution order is found: C_n-alkyl propanoate < C_n-alcohol < C_{n-4}-alkyl 3-chloropropanoate < C_{n-2}-alkyl 2-chloropropanoate (chain length $n \geqslant 6$). As shown, C_1–C_4 alcohols are eluted earlier than the corresponding *n*-alkyl propanoates, but for longer chain lengths (C_5–C_{18}) the elution order is reversed (Fig. 2). As previously shown, a significant increase in the retention occurs with the ω-chloro isomers as compared with the other isomers, particularly on polar columns[3,7,8]. Thus, Fig. 2 shows that even propyl 2-chloropropanoate was eluted earlier than methyl 3-chloropropanoate on OV-351.

For *n*-tetradecane on OV-351 a relatively short retention time is observed, the compound being partly overlapped with butyl 2-chloropropanoate. On SE-30 nearly twice as long a retention time is found, the compound being overlapped with heptyl 3-chloropropanoate (Fig. 1). The relative retention times of the compounds, relative to *n*-tetradecane, on SE-30 varied between 0.11 and 1.93 and on OV-351 between 0.27 and 3.93 (Table I).

Previously, the isothermal GC behaviour of long-chain alcohols and their derivatives has been studied by VandenHeuvel *et al.*[16] on packed columns, coated with CNSi, SE-52 and F-60-Z stationary phases. According their results, *n*-dodecanol, *n*-tetradecanol and *n*-hexadecanol were eluted from all columns earlier than the corresponding *n*-alkyl propanoates. Even the corresponding *n*-alkyl acetates were eluted after the free alcohols on SE-52 and F-60-Z. The relative retention times found for *n*-C_{12}–C_{16} propanoates (relative to the corresponding alcohols) were *ca.* 1.3, 2.3 and 2.5 on CNSi, SE-52 and F-60-Z, respectively[16]. As shown in Table I, the corresponding retention times on capillary columns with temperature programming varied between 1.21 and 1.12 on SE-30, being nearly 1.00 on OV-351. With isothermal conditions at 160°C, however, the observed ratios varied between 2.24 and 2.50 on SE-30 and between 0.99 and 0.97 on OV-351.

The maximum values for butyl and ethyl propanoates are found on SE-30 and OV-351, respectively. For chlorinated propanoates the retention is maximized with

TABLE I

RETENTION DATA OF PRIMARY C_1–C_{18} STRAIGHT-CHAIN ALCOHOLS AND *n*-ALKYL PROPANOATES, 2-CHLOROPROPANOATES AND 3-CHLOROPROPANOATES ON SE-30 AND OV-351 CAPILLARY COLUMNS

Conditions as shown in Figs. 1 and 2.

Compound	*SE-30*				*OV-351*				
	*ART***	*RRT****	*RRT*****	*RRT*§*	*ART***	*RRT****	*RRT*****	*RRT*§*	*RRT*§§*
Methanol	2.32	0.11	1.00	0.68	2.92	0.27	1.00	0.97	1.26
Ethanol	2.58	0.12	1.00	0.59	3.16	0.29	1.00	0.93	1.22
1-Propanol	2.99	0.14	1.00	0.49	4.05	0.38	1.00	0.96	1.35
1-Butanol	3.82	0.18	1.00	0.45	5.52	0.51	1.00	0.99	1.45
1-Pentanol	5.31	0.25	1.00	0.48	7.47	0.69	1.00	1.01	1.41
1-Hexanol	7.49	0.35	1.00	0.55	9.61	0.89	1.00	1.02	1.28
1-Heptanol	10.03	0.47	1.00	0.62	11.81	1.09	1.00	1.02	1.18
1-Octanol	12.71	0.60	1.00	0.69	13.99	1.30	1.00	1.01	1.10
1-Nonanol	15.31	0.72	1.00	0.73	15.95	1.48	1.00	1.01	1.04
1-Decanol	17.81	0.84	1.00	0.77	17.82	1.65	1.00	1.01	1.00
1-Undecanol	20.25	0.95	1.00	0.80	19.70	1.82	1.00	1.01	0.97
1-Dodecanol	22.54	1.06	1.00	0.83	21.49	1.99	1.00	1.01	0.95
1-Tetradecanol	26.80	1.26	1.00	0.86	24.92	2.31	1.00	1.00	0.93
1-Hexadecanol	30.70	1.44	1.00	0.89	28.17	2.61	1.00	1.00	0.92
1-Octadecanol	34.21	1.61	1.00	0.91	31.31	2.90	1.00	1.00	0.92
Methyl propanoate	3.43	0.16	1.48	1.00	3.00	0.28	1.03	1.00	0.87
Ethyl propanoate	4.39	0.21	1.70	1.00	3.39	0.31	1.07	1.00	0.77
Propyl propanoate	6.13	0.29	2.05	1.00	4.21	0.39	1.04	1.00	0.69
Butyl propanoate	8.40	0.40	2.20	1.00	5.60	0.52	1.01	1.00	0.67
Pentyl propanoate	10.99	0.52	2.07	1.00	7.40	0.69	0.99	1.00	0.67
Hexyl propanoate	13.60	0.64	1.82	1.00	9.45	0.88	0.98	1.00	0.69
Heptyl propanoate	16.10	0.76	1.61	1.00	11.61	1.08	0.98	1.00	0.72
Octyl propanoate	18.53	0.87	1.46	1.00	13.80	1.28	0.99	1.00	0.74
Nonyl propanoate	20.90	0.98	1.37	1.00	15.77	1.46	0.99	1.00	0.75
Decyl propanoate	23.11	1.09	1.30	1.00	17.69	1.64	0.99	1.00	0.77
Undecyl propanoate	25.21	1.19	1.24	1.00	19.54	1.81	0.99	1.00	0.78
Dodecyl propanoate	27.22	1.28	1.21	1.00	21.36	1.98	0.99	1.00	0.78
Tetradecyl propanoate	31.03	1.46	1.16	1.00	24.82	2.30	1.00	1.00	0.80
Hexadecyl propanoate	34.48	1.62	1.12	1.00	28.10	2.60	1.00	1.00	0.81
Octadecyl propanoate	37.61	1.77	1.10	1.00	31.26	2.89	1.00	1.00	0.83

Methyl 2-chloropropanoate	5.61	0.26	2.42	1.64	6.71	0.62	2.30	2.24	1.20
Ethyl 2-chloropropanoate	7.13	0.34	2.76	1.62	7.29	0.68	2.31	2.15	1.02
Propyl 2-chloropropanoate	9.48	0.45	3.17	1.55	8.90	0.82	2.20	2.11	0.94
Butyl 2-chloropropanoate	12.07	0.57	3.16	1.44	10.89	1.01	1.97	1.94	0.90
Pentyl 2-chloropropanoate	14.62	0.69	2.75	1.33	12.98	1.20	1.74	1.75	0.89
Hexyl 2-chloropropanoate	17.11	0.81	2.28	1.26	15.00	1.39	1.56	1.59	0.88
Heptyl 2-chloropropanoate	19.55	0.92	1.95	1.21	16.91	1.57	1.43	1.46	0.86
Octyl 2-chloropropanoate	21.89	1.03	1.72	1.18	18.80	1.74	1.34	1.36	0.86
Nonyl 2-chloropropanoate	24.09	1.13	1.57	1.15	20.65	1.91	1.29	1.31	0.86
Decyl 2-chloropropanoate	26.19	1.23	1.47	1.13	22.45	2.08	1.26	1.27	0.86
Undecyl 2-chloropropanoate	28.19	1.33	1.39	1.12	24.20	2.24	1.23	1.24	0.86
Dodecyl 2-chloropropanoate	30.11	1.42	1.34	1.11	25.90	2.40	1.21	1.21	0.86
Tetradecyl 2-chloropropanoate	33.70	1.59	1.26	1.09	29.14	2.70	1.17	1.17	0.86
Hexadecyl 2-chloropropanoate	36.96	1.74	1.20	1.07	32.50	3.01	1.15	1.16	0.88
Octadecyl 2-chloropropanoate	40.01	1.88	1.17	1.06	37.03	3.43	1.18	1.18	0.93
Methyl 3-chloropropanoate	6.80	0.32	2.93	1.98	9.45	0.88	3.24	3.15	1.39
Ethyl 3-chloropropanoate	8.69	0.41	3.37	1.98	10.30	0.95	3.26	3.04	1.19
Propyl 3-chloropropanoate	11.26	0.53	3.77	1.84	12.19	1.13	3.01	2.90	1.08
Butyl 3-chloropropanoate	13.87	0.65	3.63	1.65	14.20	1.31	2.57	2.54	1.02
Pentyl 3-chloropropanoate	16.36	0.77	3.08	1.49	16.11	1.49	2.16	2.18	0.98
Hexyl 3-chloropropanoate	18.82	0.89	2.51	1.38	18.01	1.67	1.87	1.91	0.96
Heptyl 3-chloropropanoate	21.20	1.00	2.11	1.32	19.88	1.84	1.68	1.71	0.94
Octyl 3-chloropropanoate	23.45	1.10	1.85	1.27	21.70	2.01	1.55	1.57	0.93
Nonyl 3-chloropropanoate	25.59	1.20	1.67	1.22	23.50	2.18	1.47	1.49	0.92
Decyl 3-chloropropanoate	27.61	1.30	1.55	1.19	25.20	2.33	1.41	1.42	0.91
Undecyl 3-chloropropanoate	29.58	1.39	1.46	1.17	26.89	2.49	1.36	1.38	0.91
Dodecyl 3-chloropropanoate	31.45	1.48	1.40	1.16	28.51	2.64	1.33	1.33	0.91
Tetradecyl 3-chloropropanoate	34.91	1.64	1.30	1.13	31.79	2.94	1.28	1.28	0.91
Hexadecyl 3-chloropropanoate	38.10	1.79	1.24	1.10	36.04	3.34	1.28	1.28	0.95
Octadecyl 3-chloropropanoate	41.08	1.93	1.20	1.09	42.49	3.93	1.36	1.36	1.03
n-Tetradecane	21.25	1.00	0.79	0.68	10.80	1.00	0.43	0.44	0.51

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

propyl (SE-30) and ethyl (OV-351) esters (Table I). By assigning the retention times of *n*-alkyl propanoates as 1.00, it becomes evident that the relative retention times of the corresponding halogenated esters on both columns decrease with increasing chain length.

The last column in Table I shows that in general longer retention times are found on SE-30, in spite of the higher final temperature (300°C) used. In this respect, the exceptions are C_1–C_{10} alcohols and some lower chlorinated esters. In four homologous series, the retention times of 1-butanol (1.45), butyl propanoate (0.67), methyl 2-chloropropanoate (1.20) and methyl 3-chloropropanoate (1.39) constitute the greatest disparities between the non-polar and polar capillary columns used.

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