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Note

Gas–liquid chromatographic analyses

XV*. Gas chromatographic separation of methyl esters of chlorinated propenoic acids on SE-30 and OV-351 quartz capillary columns

ILPO O. O. KORHONEN
Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä 10 (Finland)
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Recently, the chlorination of propanoyl chloride has been reported to produce all eleven chlorinated propanoyl chlorides as shown by gas chromatographic (GC) analyses of the corresponding methyl esters[1]. Negligible amounts of chloropropenoyl chlorides, as a result of dehydrochlorination, were formed.

Some of the chlorinated propenoic acids and their derivatives have been used, *e.g.*, as polymerization agents, and they are important starting materials in several organic syntheses. Nevertheless, the present results appear to be the first detailed systematic GC study of all chlorinated methyl propenoates. The separation of a mixture of seven compounds was carried out on non-polar SE-30 and highly polar OV-351 quartz capillary columns under the same operating conditions. The retention data for the compounds at one isothermal and programmed column temperatures are given and the elution order is discussed.

EXPERIMENTAL

Gas chromatography

GC analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph under the following operating conditions: injector and flame-ionization detector temperatures, 275°C (hydrogen and air flow-rates 40 and 300 ml/min); nitrogen carrier gas flow-rate, 1 ml/min; splitting ratio,1:20; and chart speed, 10 mm/min. The columns used were a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.22 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 4°C/min until elution of peaks had ceased. The isothermal runs were carried out at 80°C.

Samples

Chlorinated methyl propenoates were prepared and their structures confirmed in this laboratory as described earlier[1]. A mixture of pure compounds was used for

* For Part XIV, see I. O. O. Korhonen, *Chromatographia*, in press.

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GC analyses, the elution order of the isomers on both columns used being verified by gas chromatography–mass spectrometry (GC–MS).

RESULTS AND DISCUSSION

Chromatograms of a mixture of methyl 2-chloro- (2), *cis*-3-chloro- (3c), *trans*-3-chloro- (3t), *cis*-2,3-dichloro- (23c), *trans*-2,3-dichloro- (23t), 3,3-dichloro- (33) and trichloropropenoate (233) are given in Figs. 1 and 2, separated on SE-30 and OV-351, respectively. Tables I and II give the retention data of the compounds.

Fig. 2 shows that all the isomers were separated on OV-351, whereas on SE-30 (Fig. 1) the peaks of 2 and 3t overlapped in spite of the various operating conditions used.

As previously reported for the acetate esters of chlorinated phenolic compounds[2,3], the isomers were eluted on a non-polar phase according to their degree of chlorination. Shorter retention times of the isomers were likewise found on SE-30 (Table II). On OV-351, however, the retention time for isomer 3c was nearly twice that for 3t (Fig. 2) resulting in a reversal of the elution order of 33 and 3c.

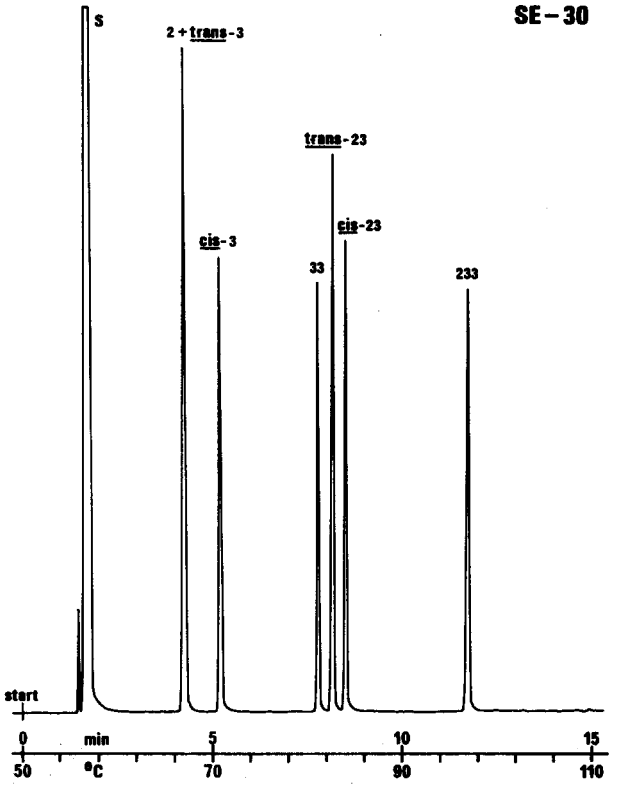


Fig. 1. Chromatogram of a mixture of chlorinated methyl propenoates, separated on an SE-30 quartz capillary column. Column temperature programmed from 50°C at 4°C/min. S = Solvent. The numbers for each isomer indicate the chlorinated positions.

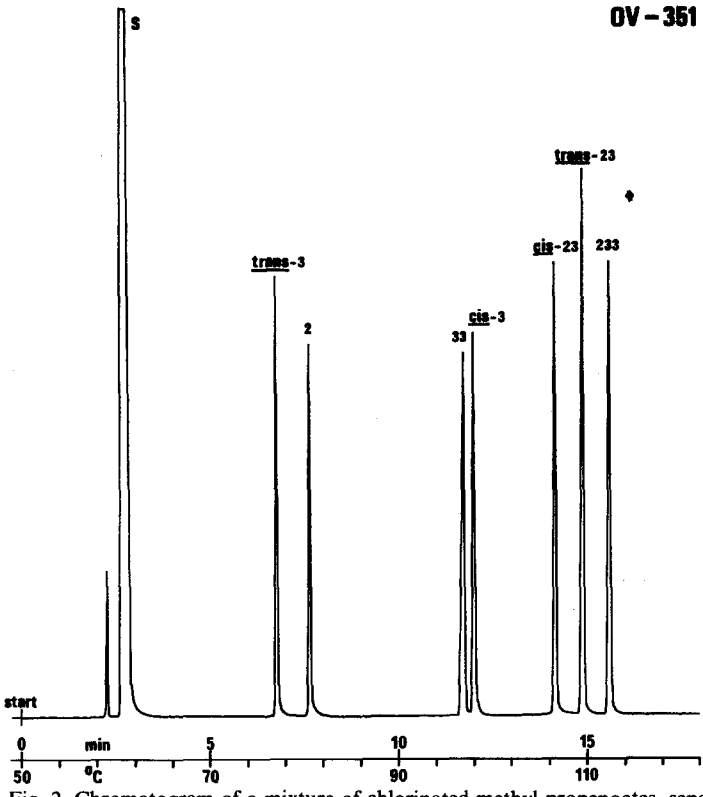
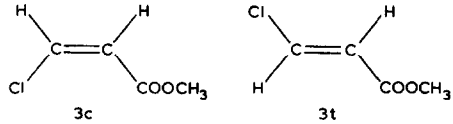


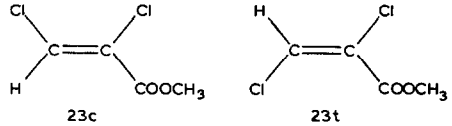
Fig. 2. Chromatogram of a mixture of chlorinated methyl propenoates, separated on an OV-351 quartz capillary column. Details as in Fig. 1.

On a polar column the order of elution is much influenced by the structures of the compounds[4]. Methyl 3-chloropropenoate and methyl 2,3-dichloropropenoate exist as *cis*- and *trans*-forms:



3c

3t



23c

23t

Compounds 3t and 23t are eluted on SE-30 before the corresponding *cis*-isomers owing to their lower boiling points. The relatively long retention time for compound 3c obtained on OV-351 is due to the strong steric hindrance between the chlorine substituent and the methoxyl group. In the isomer 3t these groups are at a con-

TABLE I

RETENTION DATA FOR CHLORINATED METHYL PROPENOATES ON AN SE-30 QUARTZ CAPPILLARY COLUMN

Methyl ester of	*Programmed from 50°C at 4°C/min*		*Isothermal at 80°C*	
	*Retention time (min)**	*RRT***	*Retention time (min)**	*RRT***
2-Chloropropenoic acid	4.21	1.00	2.61	1.00
cis-3-Chloropropenoic acid	5.15	1.22	3.11	1.19
trans-3-Chloropropenoic acid	4.21	1.00	2.61	1.00
cis-2,3-Dichloropropenoic acid	8.50	2.02	5.49	2.10
trans-2,3-Dichloropropenoic acid	8.19	1.95	5.15	1.97
3,3-Dichloropropenoic acid	7.77	1.85	4.87	1.87
Trichloropropenoic acid	11.72	2.78	9.24	3.54

* Absolute retention times (min) were measured from sample injection (*e.g.*, Fig. 1).
** Relative retention time for methyl 2-chloropropenoate taken as 1.00.

siderable distance from each other, however, and the absence of the steric hindrance results in a relatively short retention time, 3t being eluted even before 2 (Fig. 2).

Previously, Kurtz *et al.*[5] reported that a mixture of methyl *cis*- and *trans*-2,3-dichloropropenoates showed only one peak in vapour phase chromatography. As can be seen from Figs. 1 and 2, these isomers were separated both on non-polar and polar quartz capillary columns. Their separation occurred also on packed columns coated with Carbowax 20M or SE-30 stationary phases, and the isomers were even purified

TABLE II

RETENTION DATA FOR CHLORINATED METHYL PROPENOATES ON AN OV-351 QUARTZ CAPPILLARY COLUMN

Methyl ester of	*Programmed from 50°C at 4°C/min*			*Isothermal at 80°C*		
	*Retention time (min)**	*RRT***	*RRT****	*Retention time (min)**	*RRT***	*RRT****
2-Chloropropenoic acid	7.68	1.00	1.82	5.71	1.00	2.19
cis-3-Chloropropenoic acid	11.99	1.56	2.33	10.89	1.91	3.50
trans-3-Chloropropenoic acid	6.79	0.88	1.61	5.00	0.88	1.92
cis-2,3-Dichloropropenoic acid	14.11	1.84	1.66	15.03	2.63	2.74
trans-2,3-Dichloropropenoic acid	14.89	1.94	1.82	17.20	3.01	3.34
3,3-Dichloropropenoic acid	11.71	1.52	1.51	10.44	1.83	2.14
Trichloropropenoic acid	15.61	2.03	1.33	19.15	3.35	2.07

* Absolute retention times (min) were measured from sample injection (*e.g.*, Fig. 2).
** Relative retention time for methyl 2-chloropropenoate taken as 1.00.
*** Relative retention times for compounds on SE-30 taken as 1.00; for absolute retention times see Table I.

by preparative gas–liquid chromatography (GLC)[1]. The reversal of the elution order of the isomers on OV-351 is due to the stronger steric hindrance between the chlorine atom and the methoxyl group in 23t than that between the two chlorine substituents in 23c.

The relatively long retention time for compound 233 on SE-30 was in accordance with its high boiling point. On OV-351, however, 233 was eluted immediately after 23t (Fig. 2). Owing to the stabilizing effect of three chlorine substituents, there would seem to be no steric hindrance in the molecule of 233. Similarly, the geminal chlorosubstituents in compound 33 result in a shorter elution time on a polar phase. The same phenomenon has previously been reported for saturated methyl esters of chlorinated propanoic and butanoic acids[1,6–8].

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