Analysis of chlorinated acetic and propionic acids as their pentafluorobenzyl derivatives
I. Preparation of the derivatives

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Abstract

Pentafluorobenzyl (PFB) derivatives of chlorinated acetic and propionic acids were prepared adapting previously published methods to prepare PFB derivatives of non-chlorinated acids. Reaction of monochloro- and dichloroacetic acids and 2-chloro-, 2,2-dichloro- and 2,3-dichloropropionic acids with pentafluorobenzyl bromide (PFBBr) produced the PFB esters. Trichloroacetic acid reacted with PFBBr to give 1,1,1-trichloro-2-pentafluorophenylethane. On standing, this was partly degraded to 1,1-dichloro-2-pentafluorophenylethene. Gas chromatography–mass spectrometry, ^{1}H NMR and ^{13}C NMR were used to determine the structures of the derivatives.

1. Introduction

Monochloroacetic acid (MCA) and trichloroacetic acid (TCA) have mostly been analyzed by gas chromatography with electron capture detection (GC–ECD) and gas chromatography–mass spectrometry (GC–MS) as their methyl derivatives [1–3]. However, the ECD response of the methyl derivatives is not very good. Ion chromatography has been used to analyze TCA and dichloroacetic acid (DCA) in conifer needles and in rainwater [3–5]. Frank and co-workers [6,7] have reported on the use of 1-(pentafluorophenyl)diazoethane in the derivatization of the chlorinated acids.

ECD-sensitive derivatization reagents such as pentafluorobenzyl bromide [8] and p-bromophenacyl bromide [9] have been used to derivatize the organic acids, phenols and mercaptans to their esters, ethers and thioethers, respectively. According to Kawahara the ECD response for the PFB derivatives of mercaptans, phenols and organic acids is 400–1000-fold higher than their flame-ionization detection (FID) response [8].

PFBBr effectively derivatizes acids also in the presence of water [11]. The yields of the derivatization of C_1–C_{20} carboxylic acids with PFBBr are higher than 90% [11,12]. Formation of by-products or degradation of sensitive analytes due to formation of HBr [13–15] often complicates the use of PFBBr. Recently, Hofmann et al. [16] have reported on the use of pentafluorophenyldiazoalkanes as derivatization reagents to prepare PFB esters of carboxylic acids to avoid the formation of unwanted side-

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products and the problems caused by excess or decomposition of PFBBr.

The aim of the present work was to develop new and more sensitive methods for the analyses of halogenated short-chain carboxylic acids in conifer needles. The initial plan consisted of concentration and isolation of the acids by an anion-exchange resin and on-column (on-resin) derivatization by PFBBr. In the present paper the preparation of the PFB derivatives and their structure analyses by GC–MS, ^{1}H NMR and ^{13}C NMR are described.

In the literature there are several reports on the preparation of PFB derivatives of non-chlorinated (short-chain) carboxylic acids [8,13,14,17–21]. Most often, the derivatization is carried out in acetone with potassium carbonate as catalyst [8,13,20,21].

The electron ionization (EI) mass spectra of PFB derivatives of carboxylic acids usually show the molecular ion (abundance, 1–20%). Alkanoic acid derivatives show a base peak (100%) at m/z 181, which originates from the pentafluorotropylium ion $[C_7H_2F_5]^+$ and other peaks at m/z 197 (1–5%), originating from the pentafluorobenzyloxy fragment $[C_6F_5CH_2O]^+$ and at m/z 161 (7–18%) due, probably, to the loss of HF from the pentafluorobenzyl fragment [11]. The ions occurring at m/z 195 (carboxylic acids), 196 (primary amines) and 197 (carboxylic acids), can possibly be used for the qualitative discrimination between PFB derivatives of carboxylic acids, phenols and amines [11].

In negative-ion chemical ionization mass spectrometry (NICI-MS) the PFB derivatives of short-chain carboxylic acids all show a base peak at [M − 181] ($181 = C_6F_5CH_2$), originating from fragmentation of the ester to neutral 2,3,4,5,6-pentafluorobenzyl radical (M_r 181) and the carboxylate anion [M − 181]$^-$ [14,16].

2. Experimental

2.1. Preparation and spectrometric analyses of the PFB derivatives

The derivatives of chlorinated carboxylic acids were prepared by adapting the methods original-

ly used by Kawahara [8,22]. Carboxylic acids, monochloroacetic acid (Merck, >98%), dichloroacetic acid (Fluka, 99%), trichloroacetic acid (Merck, >99.5%), 2-chloropropionic acid (Koch-Light, 96%), 2,2-dichloropropionic acid (Koch-Light, 97%) and 2,3-dichloropropionic acid (Fluka, >98%), were refluxed with PFBBr (Aldrich, >99%) and K$_2$CO$_3$ in acetone for 3 h. After cooling acetone was evaporated under a gentle flow of nitrogen, the residue was dissolved in hexane and the hexane washed three times with distilled water.

GC–MS analyses of the reaction products was done with a VG AutoSpec high-resolution mass spectrometer connected to a HP 5890 Series II gas chromatograph. The column was a HP-5 (25 m × 0.2 mm I.D., 0.11 μm). The temperature program was 70°C for 1 min, increase at 10°C/min to 280°C, 280°C for 15 min). The temperature of the injector was 260°C, of the transfer line 280°C and of the ion source 260°C. The electron ionization potential was 35 eV. The GC–ECD analysis was done with a Nordion Micromat HRGC 412 gas chromatograph equipped with two 25m × 0.25 mm I.D. quartz capillary columns (NB-1701 and NB-54, 0.25 μm film thickness) and with two Ni-63 electron capture detectors. The temperature program was from 80°C to 130°C at 10°C/min, hold at 130°C for 2 min, at 2°C/min to 250°C. A JEOL GSX 270 FT-NMR spectrometer was used in the ^{1}H NMR and ^{13}C NMR measurements of the reaction products. The measuring conditions were similar to those reported previously [23–26].

3. Results and discussion

3.1. Trichloroacetic acid (TCA)

When trichloroacetic acid in acetone was refluxed with PFBBr in the presence of K$_2$CO$_3$, 1,1,1-trichloro-2-pentafluorophenylethane was produced instead of a PFB ester. On standing, the derivative, 1,1,1-trichloro-2-pentafluorophenylethane, was partly degraded to 1,1-dichloro-2-pentafluorophenylethene by cleavage of hydrogen chloride. The EI mass spectra of the derivative and its degradation product are pre-
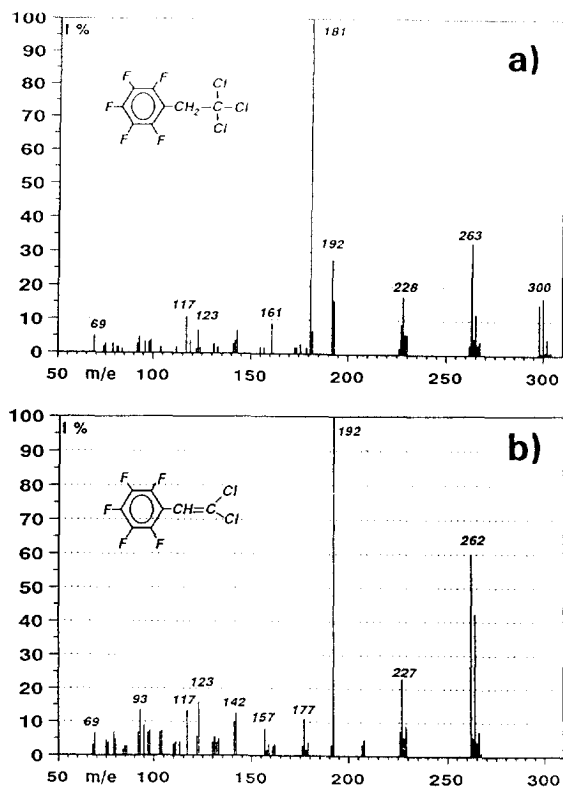
Fig. 1. Total-ion GC–EI-MS spectra of the products from the reaction of TCA with PFBBr: (a) 1,1,1-trichloro-2-penta-fluorophenylethane and (b) 1,1-dichloro-2-pentafluorophenylethene.

sented in Fig. 1. The reactions of trichloroacetic acid with PFBBr are described in Fig. 2.

3.2. Monochloroacetic acid (MCA)

The reaction of monochloroacetic acid with PFBBr produced the PFB ester of MCA in high yield. In GC–MS analyses of the product some minor peaks due to some slowly eluting unknown PFB derivatives were found as by-products.
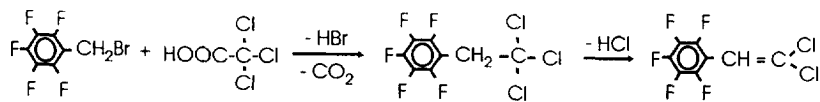
3.3. Dichloroacetic acid (DCA)

The reaction of dichloroacetic acid with PFBBr produced pure PFB ester of DCA in high yield.

3.4. 2-Chloropropionic acid (2CPA)

The PFB ester of 2-chloropropionic acid was produced with minor amounts of a PFB ester of dichloropropionic acid, probably originating from dichloropropanoic acid as an impurity in the 2-chloropropionic acid used as reagent.

3.5. Dichloropropionic acids (22DCPA and 23DCPA)

2,2-Dichloropropionic (22CDPA) acid reacted with PFBBr producing pure PFB ester of 2,2-dichloropropionic acid with a molecular mass of 322. 2,3-Dichloropropionic (23DCPA) acid reacted with PFBBr producing a mixture of the PFB ester of 2,3-dichloropropionic acid and a PFB ester of 2-chloropropenoic (2CACR, 2-chloroacrylic acid) by cleavage of HCl from the first product.

3.6. Blank syntheses

The syntheses without the acid reagent produced di(pentafluorobenzyl)ether as the only product.

3.7. Characteristics of the derivatizations

Data about the products, yields and the main MS fragments from the PFBBr derivatization of MCA, DCA, TCA, 2CPA, 22DCPA and 23DCPA are collected in Table 1. Total-ion GC–EI-MS spectra of the PFB esters obtained are presented in Fig. 3, and ^{1}H NMR and ^{13}C NMR data in Tables 2 and 3. All GC–EI-MS spectra of

Fig. 2. Reactions between pentafluorobenzyl bromide and trichloroacetic acid.

Table 1
PFBBr derivatization: products, yields and main GC–MS fragments of the derivatives

Acid	Products	M_r	Fragments	Yield (%)
MCA	PFB ester of MCA	274	181, 197, 161	50
DCA	PFB ester of DCA	308	181, 161	70
TCA	1,1,1-Trichloro-2-pentafluorophenylethane	300	181, 192, 263, 228	
	1,1-Dichloro-2-pentafluorophenylethene	262	192, 227	
2CPA	PFB ester of 2CPA	288	181, 161	100
22DCPA	PFB ester of 22DCPA	322	181, 229, 161	100
23DCPA	PFB ester of 23DCPA	322	181, 197, 216	50
	PFB ester of 2-chloro-propenoic acid (2CACR)	286	181, 197, 161	50

Table 2
^{1}H NMR chemical shifts (δ/ppm from TMS) of chlorinated carboxylic acids and their pentafluorobenzyl esters (PFBE)

Compound	Solvent	δ/ppm
MCA	^2H_2O	4.21 $(CH_2)^a$, 4.71 $(OH)^a$
MCA-PFBE	C^2HCl_3	4.20 (CH_2), 5.45 (benzyl)
DCA-PFBE	C^2HCl_3	5.96 (CH), 5.40 (benzyl)
2CPA–PFBE	C^2HCl_3	4.42 (CH), 1.70 (CH_3), 5.32 (benzyl)
22DCPA	C^2HCl_3	2.34 (CH_3), 11.69 (OH)
22DCPA-PFBE	C^2HCl_3	2.31 (CH_3), 5.49 (benzyl)
23DCPA	C^2HCl_3	4.51 (CH), 3.97, 3.86 (CH_2), 11.09 (OH)
23DCPA-PFBE	C^2HCl_3	4.43 (CH), 3.92, 3.85 (CH_2), 5.38 (benzyl)
2CACR-PFBE	C^2HCl_3	6.54, 6.07 (vinyl), 5.38 (benzyl)

[a] From the signal of trimethylsilylpropanoic acid Na-salt ($\delta = 0$ ppm).

Table 3
^{13}C NMR chemical shifts (δ/ppm from TMS) of chlorinated carboxylic acids and their pentafluorobenzyl esters (PBFE)

Compound	Solvent	δ/ppm
MCA	^2H_2O	43.86 $(CH_2)^a$, 174.44 $(CO)^a$
MCA-PFBE	C^2HCl_3	41.54 (CH_2), 55.77 (benzyl), 168.06 (CO)
DCA-PFBE	C^2HCl_3	64.93 (CH), 56.10 (benzyl), 164.12 (CO)
2CPA–PFBE	C^2HCl_3	52.22 (CH), 21.46 (CH_3), 54.89 (benzyl), 169.71 (CO)
22DCPA	C^2HCl_3	79.39 (CCl_2), 34.02 (CH_3), 172.10 (CO)
22DCPA-PFBE	C^2HCl_3	80.25 (CCl_2), 34.55 (CH_3), 56.74 (benzyl), 166.40 (CO)
23DCPA	C^2HCl_3	54.92 (CH), 43.59 (CH_2), 172.97 (CO)
23DCPA-PFBE	C^2HCl_3	55.31 (CH), 44.02 (CH_2), 166.69 (CO)
2CACR-PFBE	C^2HCl_3	126.69 $(H_2C=)$, 131.26 $(=CCl)$, 161.58 (CO)

[a] From the signal of trimethylsilylpropanoic acid Na-salt ($\delta = 0$ ppm).
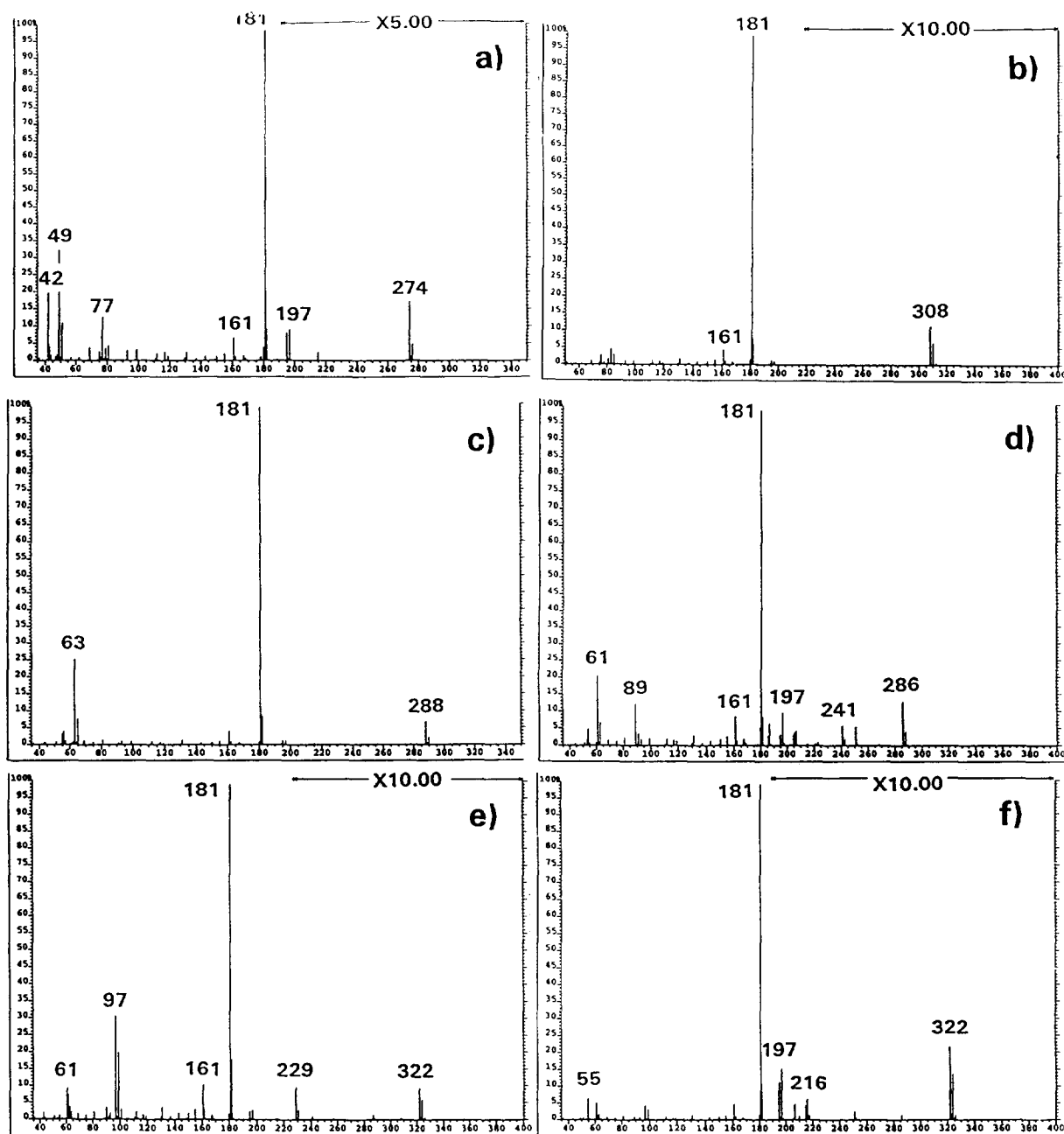Pentafluorophenyl-ring: 109.4 (C-1), 146.8 (C-2), 138.5 (C-3) and 143.1 (C-4) ppm.

Fig. 3. Total-ion GC–EI-MS spectra of the PFB esters of (a) monochloroacetic acid, (b) dichloroacetic acid, (c) 2-chloropropionic acid, (d) 2-chloropropenoic acid, (e) 2,2-dichloropropionic acid and (f) 2,3-dichloropropionic acid.

the PFB derivatives of the compounds studied showed a base peak at m/z 181 (100%). The molecular peak was about 1–14%.

The yields in the derivatization were found to be very high for chlorinated propionic acids, near 100%. For MCA the average yield from more than 20 experiments was about 50% and for DCA about 70%. The derivatives were

stable, no degradation was observed during storage of several months in a refrigerator at +4°C. The ECD response of the PFB derivatives was quite high. MCA, DCA, 2CPA and 22DCPA could be detected as their PFB derivatives at pg level (1–5 pg) without difficulties.

Acknowledgement

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