Analysis of Sulfoxylated Methyl Esters (Φ-MES): Sulfonic Acid Composition and Isomer Identification

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ABSTRACT: Derivatization of a $C_{12}\Phi$-methyl ester sulfonic acid by using iodide-trifluoroacetic anhydride in dimethylformamide in a one-step reaction yielded derivatized sulfonic thiotrifluoroacetates. The latter have been analyzed by gas chromatography–mass spectrometry (MS) and liquid chromatography–MS techniques so that, for the first time, the acid composition and the mono sulfonic acid isomer distribution are shown.

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KEY WORDS: $C_{12}\Phi$-sulfoxylated methyl ester, composition, derivatization, isomer identification.

In our previous work (1), a $C_{16}\Phi$-methyl ester sulfonic acid (Φ-MES C_{16}) sample was derivatized by methylation with trimethylorthoacetate in excess to give the dimethylester sulfonate. Different analytical techniques were used to analyze the sample, such as gas chromatography (GC)–mass spectrometry (MS), ^{1}H nuclear magnetic resonance (NMR), liquid secondary ionization mass spectrometry (LSIMS), and tandem MS. The main conclusions drawn from that investigation were as follows: (i) The SO_3 group was positioned randomly. (ii) GC–MS showed the presence of at least 11 isomers that could not be characterized. (iii) ^{1}H NMR indicated that the major species present contained one $CHSO_3$ and one CH_2CO_2 group, confirmed the presence of different isomers, and suggested the presence of polysulfonates. (iv) LSIMS and LSIMS/MS confirmed the presence of $CH_3(CH_2)_mCH(SO_3Me)(CH_2)_nCH_2CO_2Me$ (M.W. = 364 where m + n = 12); very little α or β substitution; and the presence of polysulfonated species of the forms $CH_3(CH_2)_mCH(SO_3Me)(CH_2)_nCH(SO_3Me)(CH_2)_pCH_2CO_2Me$ and $CH_3(CH_2)_mC(SO_3Me)_2(CH_2)_nCH_2CO_2Me$.

Probably as a result of the instability of the derived methyl esters, the research (1) could not be completed and the identification of each isomer remained a goal to be reached.

Therefore, in the present investigation a C_{12} fatty acid methyl ester was sulfoxidized with SO_2, O_2, and ultraviolet light of 257.3 nm wavelength as described previously (2). The sulfonic acid was further extracted from the reactor outlet product with *n*-hexane as described previously (3), and a different derivatization technique was applied using potassium iodide and trifluoroacetic anhydride (TFAA) (4).

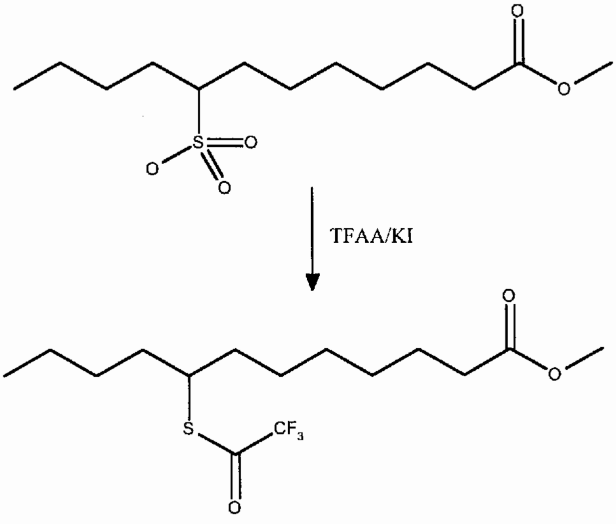
Although the random position hypothesis was confirmed for Φ-MES C_{16} (1), the present work describes the sulfonic acid composition and identifies each positional isomer for the first time by means of GC–MS and liquid chromatography (LC)–MS.

EXPERIMENTAL PROCEDURES

Derivatization of Φ-MES C_{12}. According to a method developed by Li and Lin (5) and applied by Pratesi *et al.* (4), a sulfonic acid methyl ester sample, obtained through sulfoxidation (2) and further hexane extraction (3), was derivatized by the TFAA/potassium iodide method (4), and the derivatives were analyzed by GC–MS and LC–MS [electrospray ionization (ESI) source].

In this procedure (4), the sulfonic group is first reduced to an alkyl-thiol group. Then the trifluoroacetic acid group is added to yield the thiotrifluoroacetate derivative (Scheme 1).

Derivatization procedure. Approximately 0.1 mmol of sulfonic acid methyl ester and 1 mmol of potassium iodide



SCHEME 1. Derivatization of sulfonic acid methyl ester with trifluoroacetic anhydride (TFAA) in the presence of potassium iodide. Only one possible isomer is depicted.

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Abbreviations: ESI, electrospray ionization; GC, gas chromatography; LC, liquid chromatography; LSIMS, liquid secondary ionization mass spectrometry; Φ-MES, sulfonate or sulfoxylate methyl ester obtained by sulfoxidation; MS, mass spectrometry; TFAA, trifluoroacetic anhydride; TTFA, thiotrifluoroacetyl.

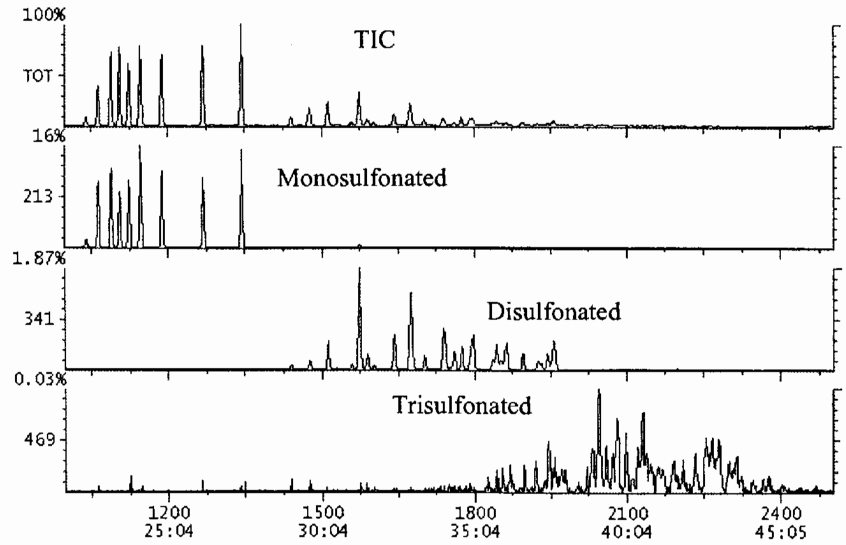

FIG. 1. Total ion chromatogram (TIC) and selected ion mass chromatograms of C_{12}-Φ-MES-TTFA (thiotrifluoroacetyl derivatives). The selected masses at *m/z* 213, 341, and 469 correspond to $[M\text{-}CF_3\text{-}COS\text{-}]^+$ of mono-, di-, and trisulfonated molecules. On the x-axis, upper numbers are scan numbers; lower numbers are elution times (min).

were dissolved in 2 mL of dimethylformamide. TFAA (1 mmol) was then added, and the solution immediately became dark. After reacting at 60°C for 2 to 3 h, the reaction was stopped by addition of 500 to 700 µL of sodium thiosulfate (5% aqueous), which quenches the iodine. The derivatized products were then extracted into 1 mL of hexane.

GC conditions. A DB-5MS capillary column (J&W Scientific, Folsom, CA; 30 m × 0.25 mm i.d., 0.25 µm film thickness) was used with a temperature program of 120°C (1 min), 2°C/min to 200°C, hold 3 min at 200°C, 3°C/min to 280°C; injector temperature: 280°C; detector type: flame ionization; temperature: 280°C.

MS conditions. GC–MS analyses were performed using a Finnigan GCQ mass spectrometer, in which the ion source is separated from the ion trap. The ion source temperature was set at 200°C. Mass spectra were acquired in the electron impact mode (70 eV) with a scan range of *m/z* 50 to 607 and a scan time of 0.5 s/scan. Liquid chromatography (LC)–MS analyses were done with a Finnigan LCQ mass spectrometer equipped with an ESI source. LC–MS spectra were acquired by direct infusion of a methanolic sample.

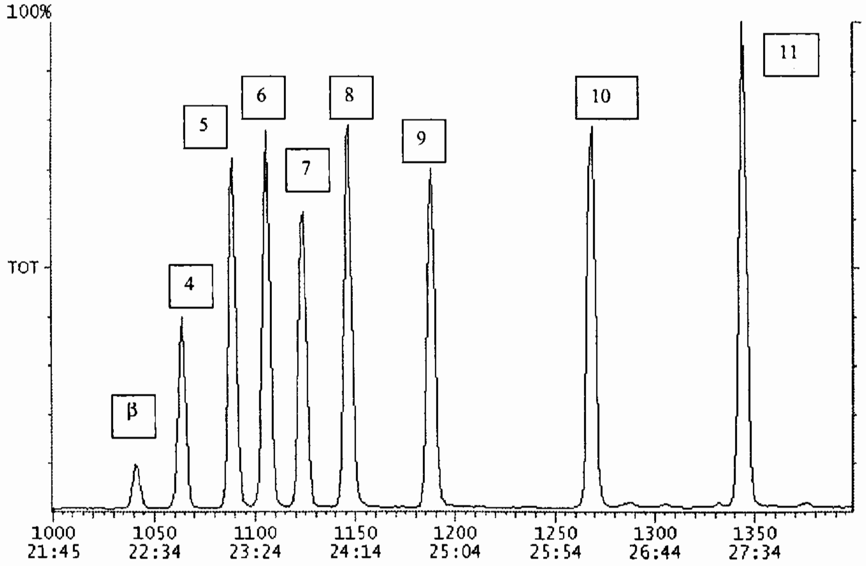

FIG. 2. Gas chromatography–mass spectrometry chromatogram showing nine positional isomers of C_{12}-Φ-MES after the trifluoroacetic anhydride/KI derivatization reacton. For experimental conditions see the Experimental Procedures section. For an explanation of values on the x-axis see Figure 1.

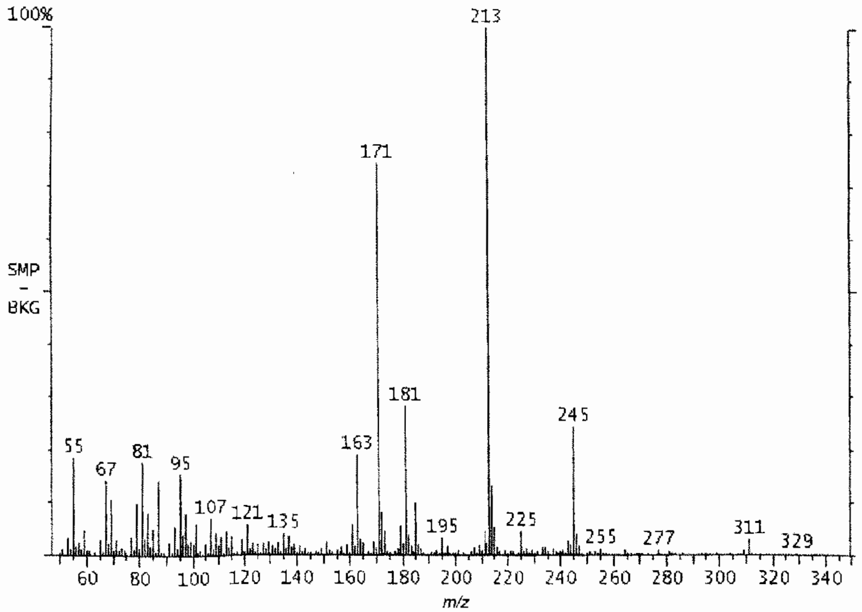

FIG. 3. Mass fragmentation of the β isomer.

RESULTS AND DISCUSSION

The total ion chromatogram and selected ion mass chromatograms of C_{12}-Φ-MES-TTFA (thiotrifluoroacetyl derivatives) are shown in Figure 1. The selected masses at *m/z* 213, 341, and 469 correspond to $[M\text{-}CF_3\text{-}COS\text{-}]^+$ of mono-, di-, and trisulfonated molecules. If we assume the same response factor among the different sulfonates, the composition of C_{12}-Φ-MES is as follows: 69% mono-, 28% di-, and 3% trisulfonates, reflecting *m/z* 213, 341, and 469, respectively.

The peaks corresponding to monosulfonate TTFA are expanded in Figure 2, where only nine peaks are observed. Because there are 11 positions along the alkyl chain, this observation means that two positions are not sulfonated. Unfortunately, the mass spectra of these peaks do not contain any fragmentation that is diagnostic to assess the position of the sulfonic group on the alkyl chain. One of these spectra, corresponding to the β position isomer (the smallest one), is shown in Figure 3. As can be observed, the main fragment corresponds to *m/z* 213.

In the sulfoxidation reaction, the main step is radical production, unlike the α-MES traditional sulfonation that proceeds through an electrophilic substitution. According to the radical mechanism, the radical formation becomes easier the farther away the CH_2 group is from $C(O)\text{-}OCH_3$ as a result of the inductive effect of the latter. Thus, no α and very little β substitution is observed. The GC data support this theory, as on nonpolar GC columns higher retention times correspond with the degree of external substitution (at the end of an alkyl chain). Accordingly, peak 11 in Figure 2 is assigned to methyl laurate 11-sulfonate, peak 10 to methyl laurate 10-sulfonate, and so on until peak 3, which is assigned to methyl laurate 3-sulfonate. The position 2 is excluded for electronic effects, as already mentioned, and position 12 for kinetic reasons. The isomeric distribution is as follows: isomer (wt%): β (= 3) (1.4); 4 (6.4), 5 (11.8), 6

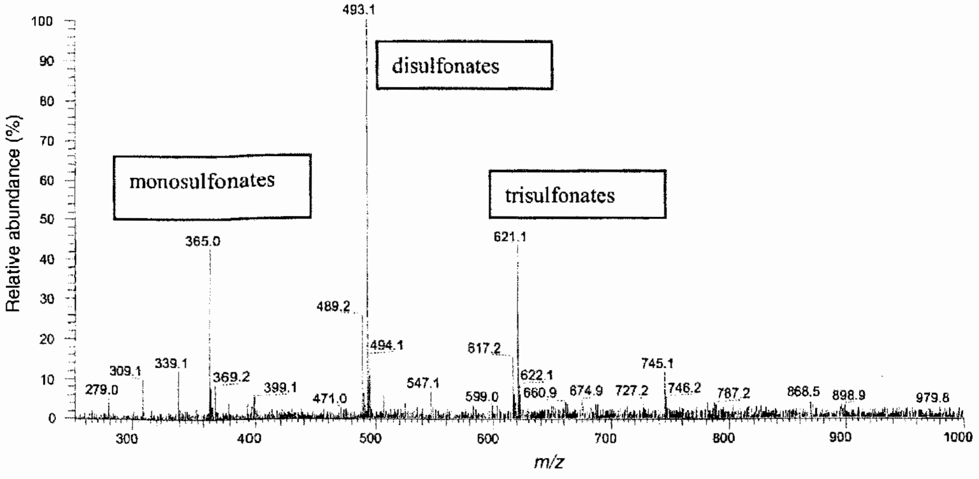

FIG. 4. Electrospray ionization mass spectrum of C_{12}-Φ-MES-TTFA (thiotrifluoroacetyl derivatives).

(12.8), 7 (10.8), 8 (13.3), 9 (12.2), 10 (14.7), 11 (16.5). As observed, the distribution can be quantitatively considered as random, except for isomer numbers 3 and 4.

The presence of mono-, di-, and trisulfonates in the sample was also confirmed by LC–MS analyses by ESI with direct infusion (without high-performance LC separation). The result is shown in Figure 4. The masses at *m/z* 365, 493, and 621 correspond to Na^+ adducts of monosulfonated, disulfonated, and trisulfonated molecules (TTFA derivatives). The peak intensities of the LC–MS or GC–MS peaks do not reflect the abundances of the different sulfonated species. Quantification is possible only if standards are available. Both GC–MS and LC–MS confirm the presence of mono-, di-, and trisulfonates in C_{12}-Φ-MES-TTFA (TTFA derivatives).

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