

Hydrogen and Trimethylsilyl Transfers During EI Mass Spectral Fragmentation of Hydroxycarboxylic and Oxocarboxylic Acid Trimethylsilyl Derivatives

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This paper, describing electron ionization mass spectral fragmentation of some hydroxycarboxylic and oxocarboxylic acid trimethylsilyl derivatives, focuses on the formation of fragment ions resulting from the interactions between the two functionalities of these compounds. These interactions result in the formation of fragment ions at $[\text{CH}_2 = \text{C}(\text{OTMS})_2]^+$, $[\text{CH}_2 = \text{CHC}(\text{OTMS}) = \text{OTMS}]^+$, $[\text{M} - 31]^+$, $[\text{M} - 105]^+$, and $[\text{M} - \text{RCHO}]^+$ in the case of hydroxycarboxylic acid trimethylsilyl derivatives of formula $\text{RCHOTMS}(\text{CH}_2)_n\text{COOTMS}$ and at $[\text{RC}(\text{OTMS}) = \text{CH}_2]^+$, $[\text{RC}(=\text{OTMS})\text{CH} = \text{CH}_2]^+$, and $[\text{M} - \text{RC}(=\text{O})\text{CH}_2]^+$ in the case of oxocarboxylic acid trimethylsilyl esters of formula $\text{RC}(=\text{O})(\text{CH}_2)_n\text{COOTMS}$. Some of these fragmentations appeared to be sufficiently specific to be used to characterize these compounds. Several fragmentation pathways involving trimethylsilyl and hydrogen transfers were proposed to explain the formation of these different fragment ions and were substantiated by deuterium labeling. (J Am Soc Mass Spectrom 2008, 19, 66–75) © 2008 American Society for Mass Spectrometry

Silylation is by far the major derivatization procedure for GC/MS analyses [1–3]. Silyl derivatives are formed when active proton displacement (in –OH, –SH, or –NH groups) by an alkylsilyl group occurs. The most common silylation procedure is trimethylsilylation. Trimethylsilyl derivatives combine thermal stability and high volatility. In general, electron ionization (EI) mass spectra of trimethylsilyl ethers or esters exhibit a significant $[\text{M} - 15]^+$ ion formed by loss of a methyl group bonded to silicon, which is very useful in determining the molecular mass. It is very important to note that EI mass spectra of trimethylsilyl derivatives may be employed not only for molecular weight determinations, but also for structural deductions [4].

Trimethylsilyl group migrations during EI fragmentation process are common [5, 6] and take place by means of ion-neutral complexes [7]. These rearrangements are generally considered useful for deducing structures of unknown spectra [8]; however, in some cases, misleading conclusions may be drawn. Though trimethylsilyl group migrations usually occur through five- to eight-member-ring transition states [9], intense long-range migration of the trimethylsilyl group was

previously observed in the case of trimethylsilyl derivatives of some steroid compounds [8, 10–13]. The capability of the trimethylsilyl group to migrate over a wide range of distances was also demonstrated in the case of semirigid or rigid molecules [5]. Recently, a significant transfer of trimethylsilyl group towards the carbonyl group was also observed during EI fragmentation of the trimethylsilyl derivatives of long-chain ω -hydroxycarboxylic and ω -dicarboxylic acids [14], showing that such migrations may also occur in the case of nonrigid structures.

Hydrogen transfers between distant functionalities during EI fragmentation processes are also well known [6, 15, 16], for this reaction hydrogen activation is needed and is caused by groups such as keto, amino, ether, trimethylsilyloxy, as well as by chain branching and unsaturation.

In the present work, which is a part of a more general study of the synergistic effects during EI mass fragmentation of polyfunctional compounds [14, 17–19], we describe EI mass spectral fragmentation of several hydroxycarboxylic and oxocarboxylic acid trimethylsilyl derivatives, which involves trimethylsilyl and hydrogen transfers.

The characterization of such compounds appears to be of great environmental importance [20, 21]. Indeed, it was previously demonstrated that autoxidative processes could induce a bias during alkenone-based pa-

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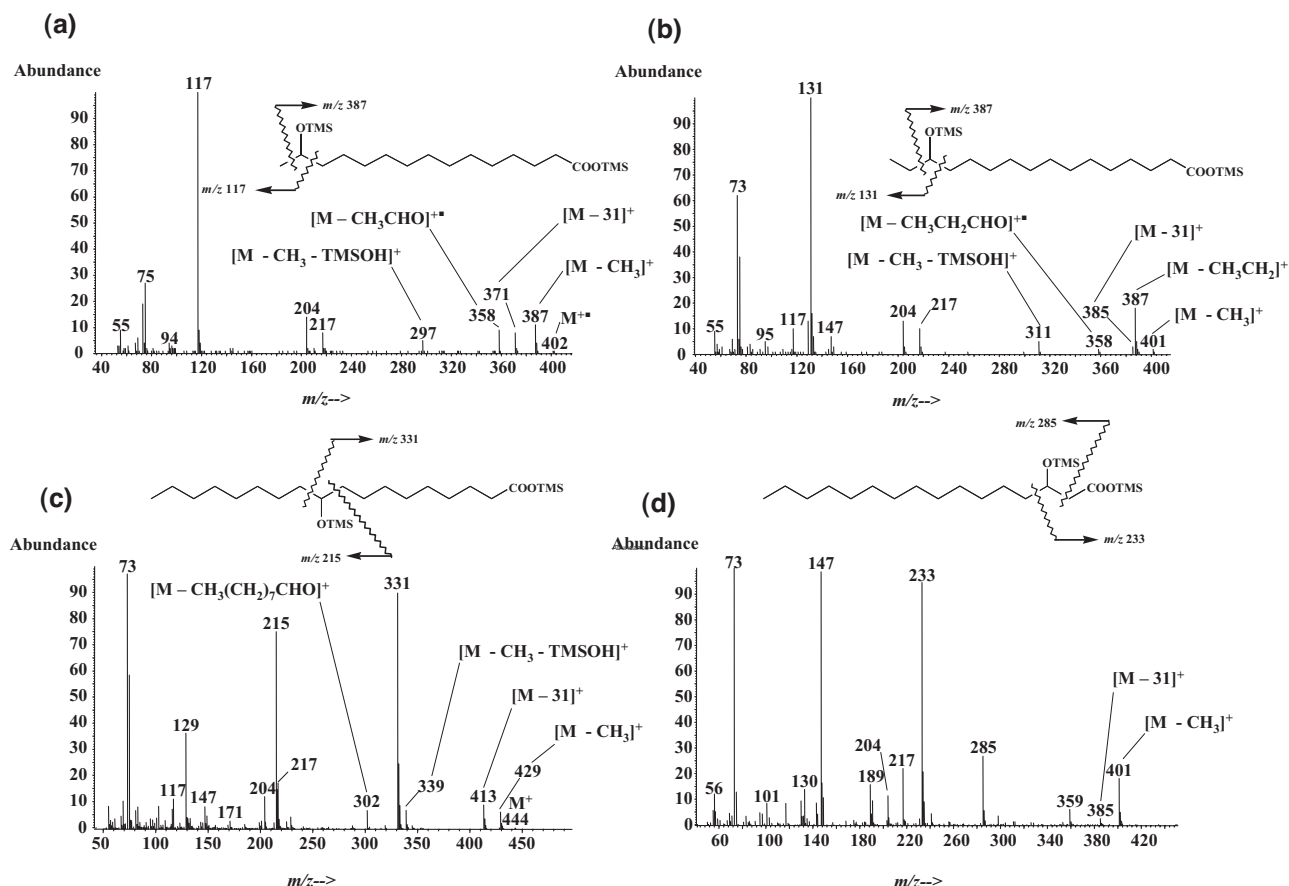


Figure 1. EI mass spectra of (a) 14-hydroxypentadecanoic, (b) 14-hydroxyhexadecanoic, (c) 10-hydroxyoctadecanoic, and (d) 3-hydroxyhexadecanoic acid trimethylsilyl derivatives.

leotemperature estimations [20]. The allylic hydroperoxyketones thus formed are cleaved homolytically and heterolytically in seawater, affording several (ω -1)- and (ω -2)-oxocarboxylic acids [21]. These compounds and the corresponding hydroxyacids produced after subsequent NaBH_4 -reduction were proposed as specific markers of alkenone autoxidative alterations in seawater [21]. It is thus essential to be able to differentiate these compounds from isobaric fatty acids or diols, respectively.

To generalize our conclusions, shorter hydroxycarboxylic and oxocarboxylic acids derived from the oxidation of fatty acids were also investigated.

Experimental

Chemicals

3-Hydroxyhexadecanoic, 3-hydroxyoctadecanoic, and 6-oxoheptanoic acids were obtained from Sigma-Aldrich. (ω -1)- and (ω -2)-Oxocarboxylic acids ranging from C_{14} to C_{16} were obtained by heterolytic cleavage of autoxidation products of C_{37} and C_{38} alkenones [20, 21]. NaBH_4 reduction of these oxoacids then afforded the corresponding (ω -1)- and (ω -2)-hydroxycarboxylic acids. 8-Hydroxyoctadec-9-enoic, 10-hydroxyoctadec-

11-enoic, 10-hydroxyoctadecanoic, 11-hydroxyoctadecanoic, 12-hydroxyoctadecanoic, 9-oxooctadecanoic, 10-oxooctadecanoic, and 9-oxooctadec-10-enoic acids were prepared according to previously described procedures [22]. 9-Oxodecanoic acid resulted from hydration and retro-aldolization (alkaline hydrolysis) of 9-oxooctadec-10-enoic acid. NaBD_4 reduction of 10-oxooctadecanoic acid afforded (10- D_1)-10-hydroxyoctadecanoic acid. Deuteration of 10-oxooctadecanoic acid in the α -positions relative to the carbonyl group was carried out according to classic deuterium exchange procedure [23]. Production of a mixture of (11- D_1)-12-hydroxyoctadecanoic and (12- D_1)-11-hydroxyoctadecanoic acids in low yields required two steps: (1) epoxidation of vaccenic acid with 3-chloroperoxybenzoic acid in dry methylene chloride and (2) subsequent reduction of the foregoing epoxide with excess of NaBD_4 in diethyl ether/methanol.

Silylation

Compounds (1 mg) to be silylated were taken up in 300 μL of a mixture of pyridine and BSTFA (*N,O*-Bis(trimethylsilyl)trifluoroacetamide, Supelco Inc., St Quentin Fallavier, France) (2:1, vol/vol) and allowed to react at

Table 1. Characteristic mass spectral fragments of some hydroxyacid trimethylsilyl derivatives

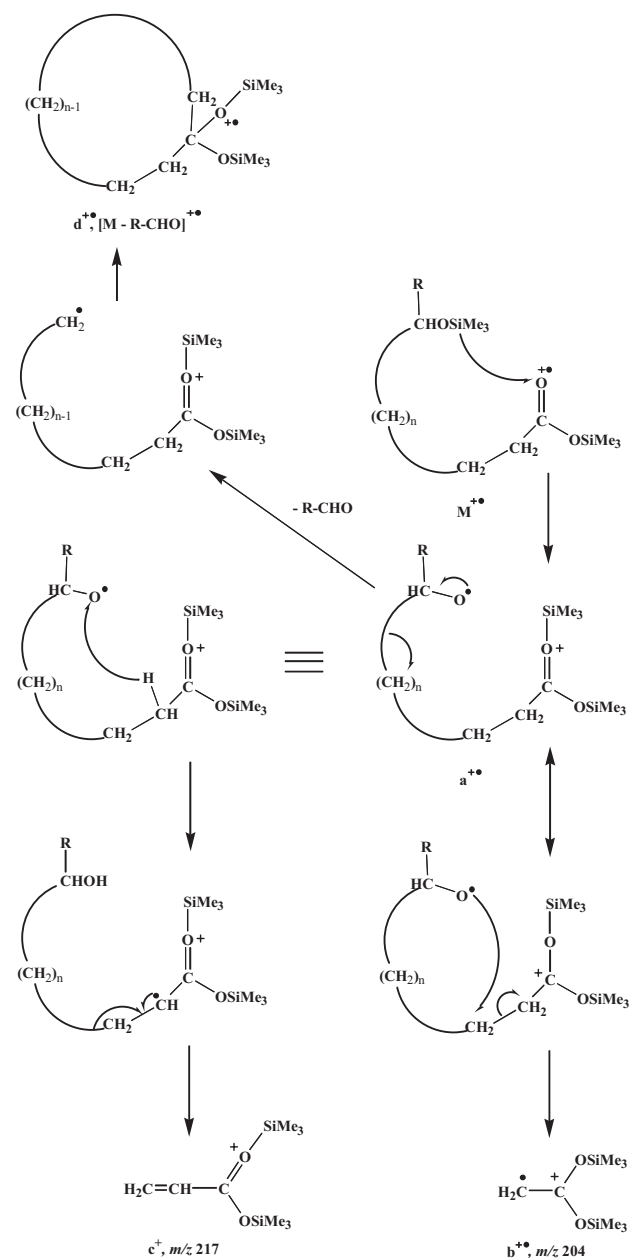
Compound	α -cleavage 1 ^a m/z (%) ^b	α -cleavage 2 ^a m/z (%)	m/z 204 (%) ^b	m/z 217 (%)	[M - 105] ⁺ (%)	m/z	[M - RCHO] ⁺ m/z (%)	[M - 31] ⁺ m/z (%)	[M - CH ₃] ⁺ m/z (%)
13-Hydroxytetradecanoic acid	117 (100%) ^c	373 (6%)	6%	7%	283 (3%)	344 (5%)	357 (3%)	-	-
14-Hydroxypentadecanoic acid	117 (100%) ^c	387 (11%)	12%	9%	297 (6%)	358 (7%)	371 (6%)	-	-
15-Hydroxyhexadecanoic acid	117 (100%) ^c	401 (6%)	14%	10%	311 (6%)	372 (5%)	385 (4%)	-	-
12-Hydroxytetradecanoic acid	131 (93%)	359 (23%)	4%	7%	283 (4%)	330 (4%)	357 (6%)	-	-
13-Hydroxypentadecanoic acid	131 (100%)	373 (50%)	13%	12%	297 (9%)	344 (6%)	371 (9%)	-	-
14-Hydroxyhexadecanoic acid	131 (100%)	387 (50%)	16%	12%	311 (8%)	358 (6%)	385 (10%)	-	-
15-Hydroxyheptadecanoic acid	131 (87%)	401 (37%)	14%	12%	325 (8%)	372 (5%)	399 (6%)	-	-
10-Hydroxyoctadecanoic acid	215 (79%)	331 (98%)	12%	17%	339 (7%)	302 (9%)	413 (10%)	428 (1%)	428 (1%)
11-Hydroxyoctadecanoic acid	201 (69%)	345 (78%)	5%	22%	339 (4%)	316 (11%)	413 (10%)	428 (3%)	428 (1%)
12-Hydroxyoctadecanoic acid	187 (72%)	359 (36%)	4%	12%	339 (3%)	330 (5%)	413 (4%)	-	-
3-Hydroxyoctadecanoic acid	233 (100%)	313 (19%)	10% ^d	19%	339 (2%)	204 (10%) ^d	413 (4%)	-	-
10-Hydroxyhexadecanoic acid	233 (100%)	285 (26%)	12% ^d	22%	311 (2%)	204 (12%) ^d	385 (4%)	-	-
10-Hydroxyoctadec-11-enoic acid	213 (100%)	-	4%	5%	337 (2%)	302 (7%)	411 (4%)	-	-
8-Hydroxyoctadec-9-enoic acid	241 (100%)	-	3%	9%	337 (1%)	274 (10%)	411 (4%)	-	-

^aRelative to the TMS ether group.^bRelative abundance.^cIn these cases the fragment ion at m/z 117 also corresponds to α -cleavage relative to the TMS ester group.^dIsobaric fragment ions.

50 °C for 1 h. After evaporation to dryness (to eliminate pyridine), the residue was dissolved in ethyl acetate (2 mL/mg) and BSTFA (0.1 mL) (to avoid desilylation) and analyzed by gas chromatography/mass spectrometry (GC/MS).

Mass Spectrometry

Analyses by gas chromatography/electron impact mass spectrometry were performed with a Hewlett Packard HP 5890 series II plus gas chromatograph connected to a HP 5972 mass spectrometer (Agilent Technologies, Massy, France). The following opera-



Scheme 1. Proposed formation pathways of ions b^+ (at m/z 204), c^+ (at m/z 217), and d^+ $[M - RCHO]^+$ involving trimethylsilyl transfer.

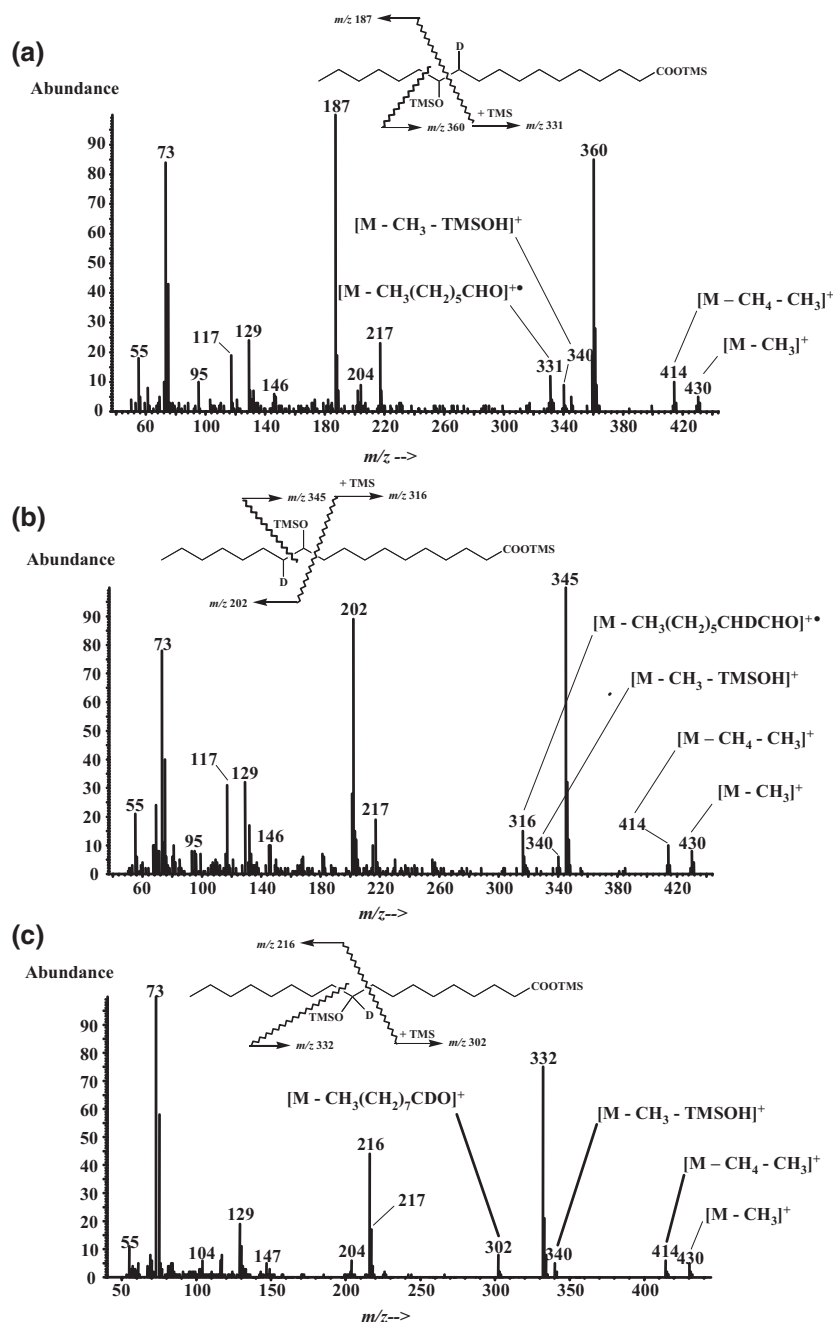


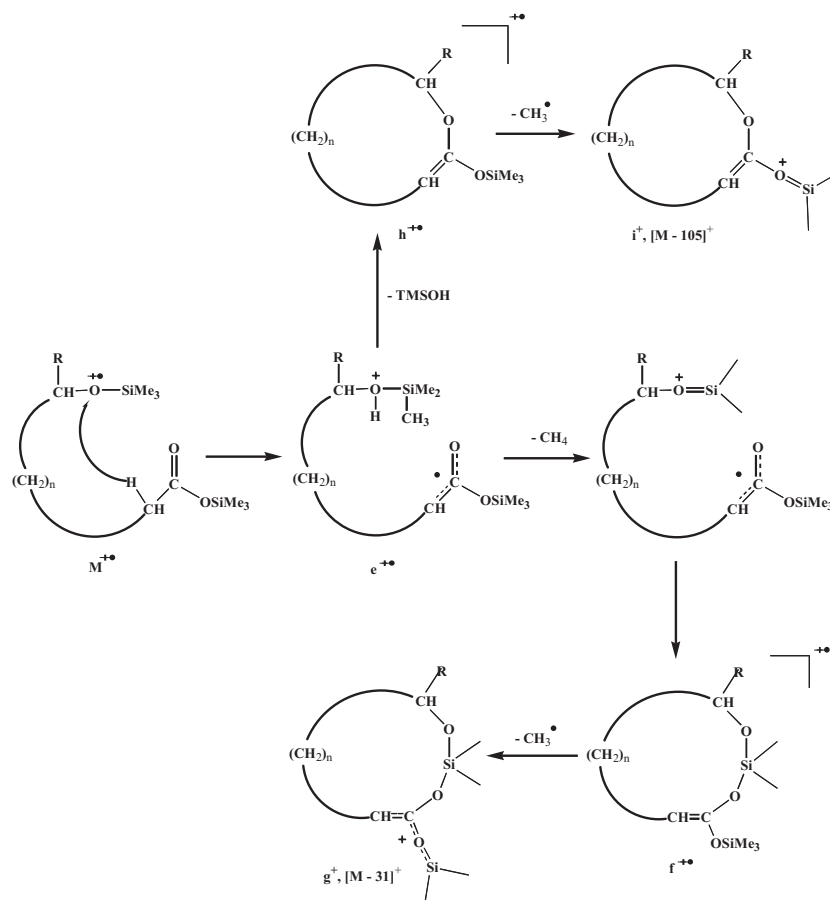
Figure 2. EI mass spectra of (a) (11-D₁)-12-hydroxyoctadecanoic, (b) (12-D₁)-11-hydroxyoctadecanoic, and (c) (10-D₁)-10-hydroxyoctadecanoic acid trimethylsilyl derivatives.

tive conditions were employed: 30 m \times 0.25 mm (i.d.) capillary column coated with SOLGEL-1 (SGE; film thickness, 0.25 μ m); oven temperature programmed from 60 $^{\circ}$ C to 130 $^{\circ}$ C at 30 $^{\circ}$ C min⁻¹ and then from 130 $^{\circ}$ C to 300 $^{\circ}$ C at 4 $^{\circ}$ C min⁻¹; carrier gas (He) pressure was maintained at 1.04 bar until the end of the temperature program and then programmed from 1.04 bar to 1.5 bar at 0.04 bar min⁻¹; injector (on column with a retention gap) temperature, 50 $^{\circ}$ C; electron energy, 70 eV; source temperature, 170 $^{\circ}$ C; mass range, 50–700 Th; cycle time, 1.5 s.

Results and Discussion

Fragmentation of Hydroxycarboxylic Acid Trimethylsilyl Derivatives

We could previously demonstrated [14] that mass spectra of ω -hydroxycarboxylic and ω -dicarboxylic acid trimethylsilyl derivatives exhibited some fragmentations that are lacking in mass spectra of compounds containing only an ester or an ether group. Most of the fragments ions thus formed resulted from trimethylsilyl



Scheme 2. Proposed formation pathways of ions \mathbf{g}^+ (at $[M - 31]^+$) and \mathbf{i}^+ (at $[M - 105]^+$) involving hydrogen transfer.

group to the ionized ester group and subsequent losses of a neutral molecule of methane and a methyl radical [14]. Indeed, the loss of methane is often observed in EI mass spectra of trimethylsilyl derivatives [24, 25]. The presence of a peak at m/z 414 (corresponding to $[M - 31]^+$) in the EI mass spectrum of (10-D₁)-10-hydroxyoctadecanoic acid trimethylsilyl derivative (Figure 2c) leads us to discard such a possibility. Indeed, the transfer of the deuterium atom from the ether group to the ionized ester group would have resulted in a shift of this peak to m/z 413 $[M - \text{CH}_3\text{D} - \text{CH}_3]^+$. We thus propose the mechanisms described in the Scheme 2 to explain the formation of these ions. This pathway involves initial hydrogen transfer from the carbon in α position relative to the ester group to the ionized oxygen atom of the ether group. The resulting distonic ion $\mathbf{e}^{+\cdot}$ (where the radical is stabilized by conjugation) may then lose a neutral molecule of methane by way of a four-membered hydrogen rearrangement with charge retention [6] to give after cyclization the radical ion $\mathbf{f}^{+\cdot}$. Subsequent loss of a methyl radical by this ion $\mathbf{f}^{+\cdot}$ yields the ion \mathbf{g}^+ at $[M - 31]^+$ stabilized by conjugation. The involvement of such a pathway is in good agreement with the presence of a peak at m/z 414 in the EI mass spectrum of (10-D₁)-10-hydroxyoctadecanoic acid trimethylsilyl derivative (Figure 2c) and is also well

supported by the presence of a weak peak corresponding to the fragment ion f^{+} at $[\text{M} - \text{CH}_3]^{+}$ in EI mass spectra of some hydroxycarboxylic acid trimethylsilyl derivatives (Table 1). The subsequent losses of a neutral molecule of trimethylsilanol and a methyl radical by the ion e^{+} (Scheme 2) constitute potential sources of the ion at $[\text{M} - 105]^{+}$; however, this ion can also be formed from the molecular ion without hydrogen transfer.

Fragmentation of Oxocarboxylic Acid Trimethylsilyl Esters

EI mass spectra of oxocarboxylic acid trimethylsilyl esters of formula $\text{RC}(=\text{O})(\text{CH}_2)_n\text{COOTMS}$ (Figure 3, Table 2) exhibit fragment ions at m/z 117, 129, 145, and $[\text{M} - \text{CH}_3]^+$ resulting from classical fragmentation of the TMS ester groups [14]. Classical γ -hydrogen rearrangement of the keto group also affords the ion $[\text{RC}(\text{OH}) = \text{CH}_2]^+$. If the keto group possesses γ -hydrogen atoms in both chains consecutive rearrangements yielding the ion $[\text{CH}_3\text{C}(\text{OH}) = \text{CH}_2]^+$ can occur. The presence of a significant peak at $[\text{M} - 33]^+$ can be attributed to successive losses of a neutral molecule of H_2O and a methyl radical. Indeed, the loss of water is often observed in EI mass spectra of long-chain ketones [6].

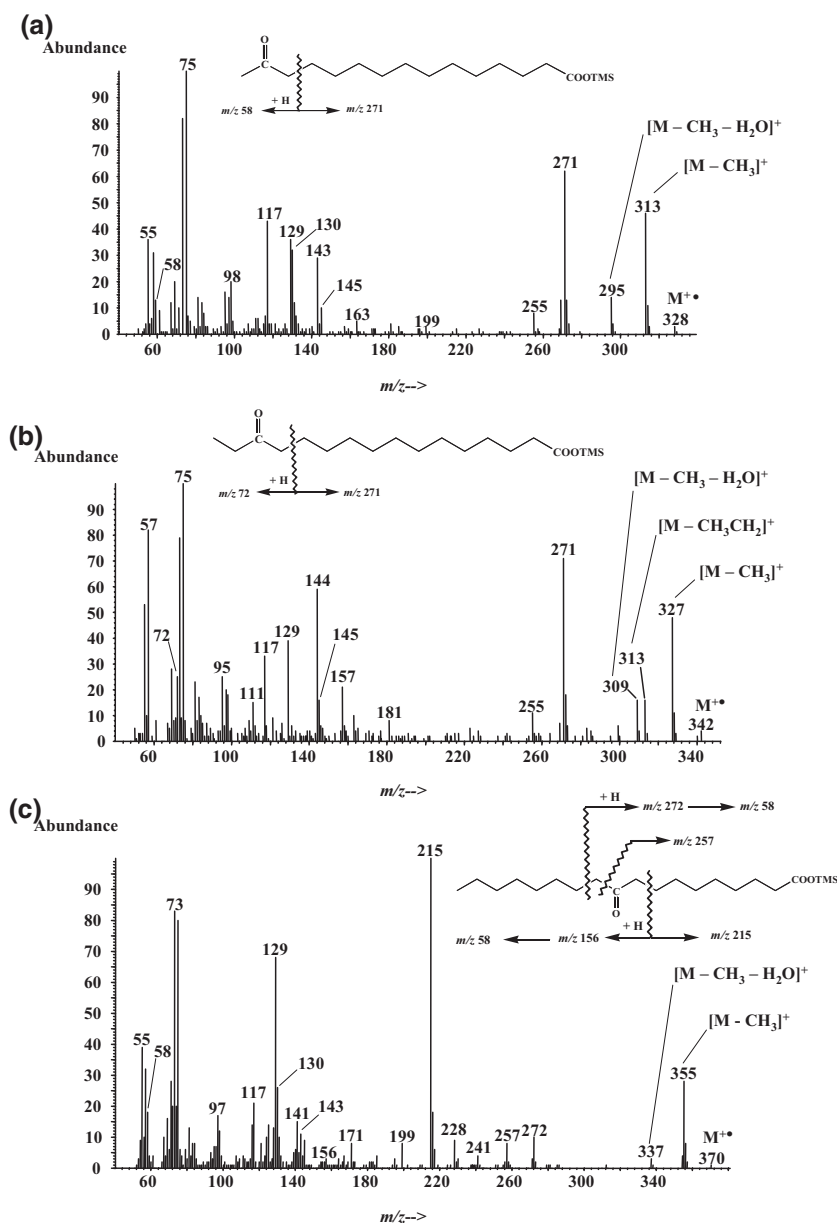


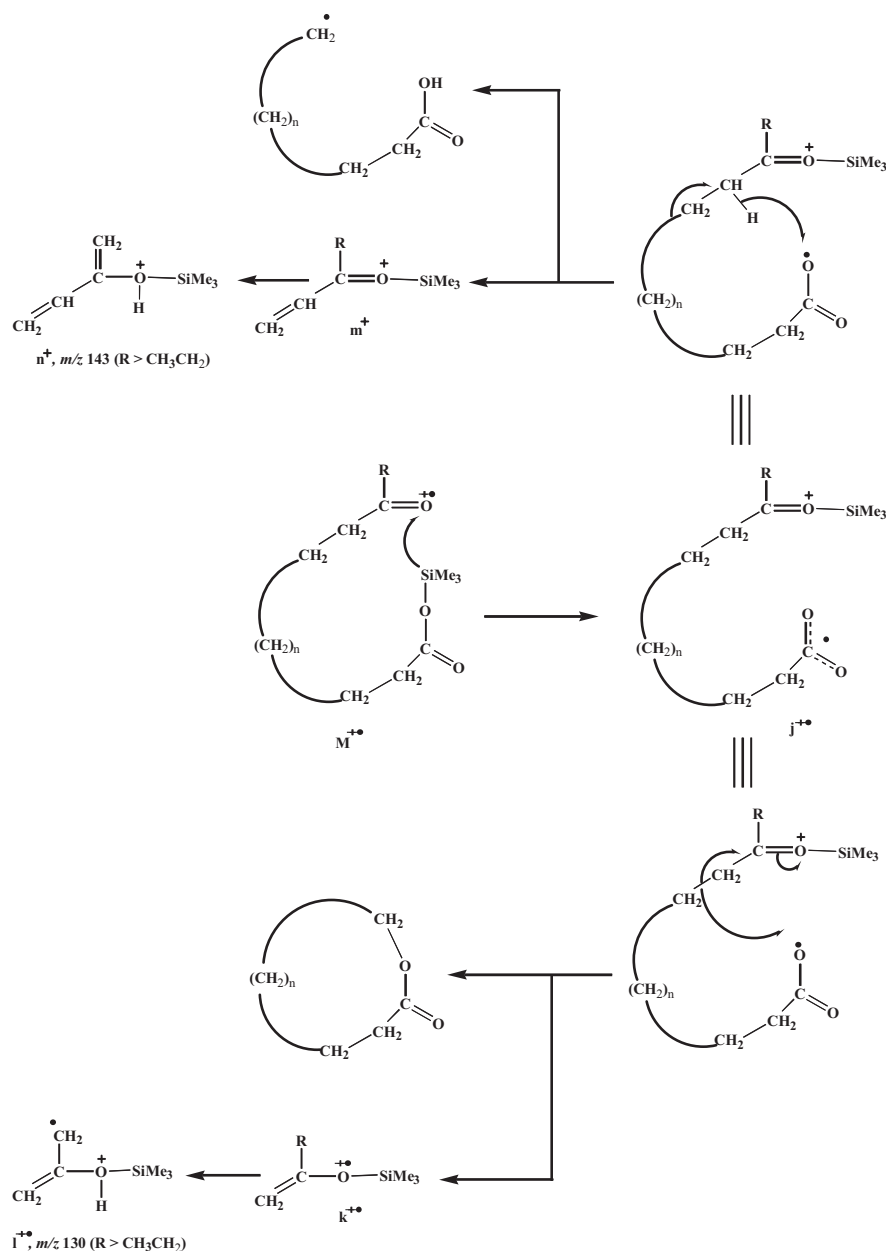
Figure 3. EI mass spectra of (a) 14-oxopentadecanoic, (b) 14-oxohexadecanoic, and (c) 10-oxooctadecanoic acid trimethylsilyl esters.

These EI mass spectra also show strong fragment ions resulting from the interactions between the keto and ester functionalities ($[RC(OTMS) = CH_2]^+$, $[RC(=OTMS)CH = CH_2]^+$ and $[M - RC(=O)CH_2]^+$) (Figure 3, Table 2). These fragment ions are lacking or present in very weak proportions in EI mass spectra of ketones [6] and TMS esters [14].

To explain the formation of the ions $[RC(OTMS) = CH_2]^+$, we propose the pathways described in Scheme 3 involving an initial trimethylsilyl transfer from the ester group to the ionized ketone. The distonic ion j^{+} thus formed may then undergo β -cleavage giving the radical ion $[RC(OTMS) = CH_2]^+$ (k^{+}). When R- has more than two carbon atoms, subsequent γ -hydrogen rearrangement of the ion k^{+} affords the ion l^{+} at m/z

130 (Figure 3c). Transfer of a hydrogen atom from the carbon in α -position relative to the ionized keto group of ion j^{+} to the carboxyl radical and subsequent γ -cleavage may afford the ion $[RC(=OTMS)CH = CH_2]^+$ (m^{+}). When R- is longer than ethyl, the ion m^{+} can then undergo γ -hydrogen rearrangement giving the ion n^{+} at m/z 143 (Figure 3c). The shift of the ions k^{+} , l^{+} , m^{+} , and n^{+} to m/z 232, 134, 244, and 146, respectively, in the mass spectrum of (9- D_2 ,11- D_2)-10-oxooctadecanoic acid trimethylsilyl ester (Figure 4) is consistent with such pathways.

We propose the fragmentation pathways described in the Scheme 4 to explain the formation of the intense fragment ions at $[M - RC(=O)CH_2]^+$ in the mass spectra of oxocarboxylic acid trimethylsilyl esters.



Scheme 3. Proposed formation pathways of ions $I^{+•}$ and n^{+} involving trimethylsilyl transfer.

These pathways involve initial hydrogen transfer from the carbon in γ -position relative to the keto group to the ionized ester group and subsequent β -cleavage relative to the keto group affording the ion o^{+} and the radical p^{+} stabilized by conjugation. These pathways are well supported by the presence of a peak at m/z 215 in the mass spectrum of (9- D_2 ,11- D_2)-10-oxooctadecanoic acid trimethylsilyl ester (Figure 4) corresponding to $[M - CH_3(CH_2)_6CD_2C(=O)CD_2]^{+}$.

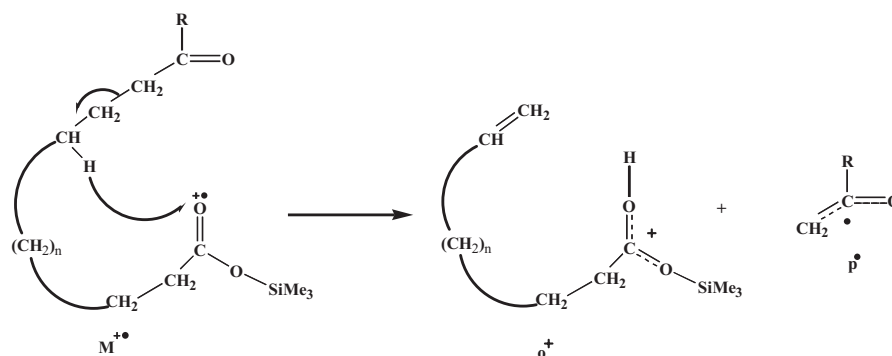
Conclusions

It is generally considered that a molecule containing two functional groups can undergo EI mass fragmentations that are not found for those with either group

alone. Examination of EI mass spectra of hydroxycarboxylic and oxocarboxylic acid trimethylsilyl derivatives allowed us to confirm this assertion.

Although mass spectra of hydroxycarboxylic acid trimethylsilyl derivatives of formula $RCHOTMS$ ($(CH_2)_nCOOTMS$) are dominated by fragment ions resulting from classic α -cleavage relative to the trimethylsilyloxy ether group, they also exhibit fragment ions at m/z 204, 217, $[M - 31]^{+}$, $[M - 105]^{+}$, and $[M - RCHO]^{+}$ resulting from trimethylsilyl and hydrogen transfers between the two functionalities of the molecule. These fragment ions could be very useful to characterize these compounds and notably to differentiate them from isobaric diol trimethylsilyl derivatives.

Mass spectra of oxocarboxylic acid trimethylsilyl



Scheme 4. Proposed formation pathways of ion o^+ at $[M - RC(=O)CH_2]^+$ involving hydrogen transfer.

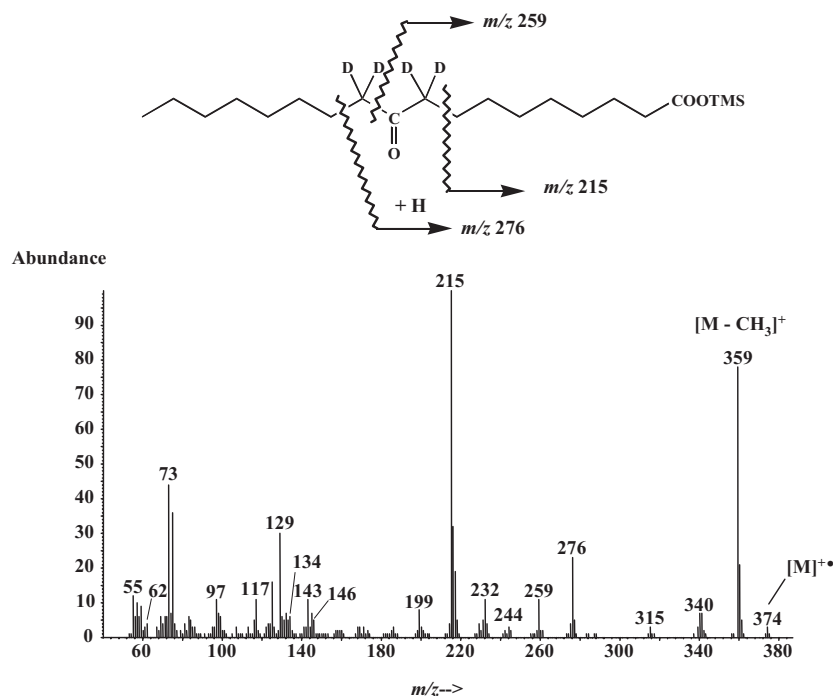


Figure 4. EI mass spectrum of (9-D₂,11-D₂)-10-oxooctadecanoic acid trimethylsilyl ester.

esters of formula $RC(=O)(CH_2)_nCOOTMS$ show fragment ions at $[RC(OTMS)=CH_2]^+$, $[RC(=OTMS)CH=CH_2]^+$, and $[M - RC(=O)CH_2]^+$ also resulting from trimethylsilyl and hydrogen transfers between the two functionalities of the molecule. These specific fragment ions could be very useful in differentiating these compounds from isobaric fatty acid trimethylsilyl esters.

Acknowledgments

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