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## Electron ionization mass fragmentation of monounsaturated long-chain $\alpha,\omega$ -dicarboxylic acid trimethylsilyl derivatives

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Keywords:	EIMS, monounsaturated dicarboxylic acids, TMS derivatives, Mass fragmentation, Neutral losses
Abstract:	<p><b>RATIONALE</b> Long-chain monounsaturated <math>\alpha,\omega</math>-dicarboxylic acids are important components of the cuticle and suberized cell walls of plants. Identification and quantification of these compounds, which are widespread in environmental samples, can be challenging.</p> <p><b>METHODS</b> The EI-MS fragmentation pathways of long-chain monounsaturated <math>\alpha,\omega</math>-dicarboxylic acid TMS derivatives were investigated. These pathways were deduced by low-energy CID-GC-EI-MS/MS and accurate mass measurement.</p> <p><b>RESULTS</b> Low-energy CID-MS/MS analyses and accurate mass measurement enabled us to elucidate EI-MS fragmentations of long-chain monounsaturated <math>\alpha,\omega</math>-dicarboxylic acid TMS derivatives. These fragmentations involves successive losses of neutral molecules of TMSOH and CO initiated by transfer of allylic hydrogen atom to the ionized ester groups, which are thus totally lacking in EI mass spectra of saturated homologues.</p> <p><b>CONCLUSIONS</b> EI-MS fragmentations of long-chain monounsaturated <math>\alpha,\omega</math>-dicarboxylic acids TMS derivatives exhibit specific fragment ions that can be very useful for the quantification in MRM mode of trace amounts of these compounds in environmental samples.</p>

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## RATIONALE

Long-chain monounsaturated  $\alpha,\omega$ -dicarboxylic acids are important components of the cuticle and suberized cell walls of plants. Identification and quantification of these compounds, which are widespread in environmental samples, can be challenging.

## METHODS

The EI-MS fragmentation pathways of long-chain monounsaturated  $\alpha,\omega$ -dicarboxylic acid TMS derivatives were investigated. These pathways were deduced by low-energy CID-GC-EI-MS/MS and accurate mass measurement.

## RESULTS

Low-energy CID-MS/MS analyses and accurate mass measurement enabled us to elucidate EI-MS fragmentations of long-chain monounsaturated  $\alpha,\omega$ -dicarboxylic acid TMS derivatives. These fragmentations involves successive losses of neutral molecules of TMSOH and CO initiated by transfer of allylic hydrogen atom to the ionized ester groups, which are thus totally lacking in EI mass spectra of saturated homologues.

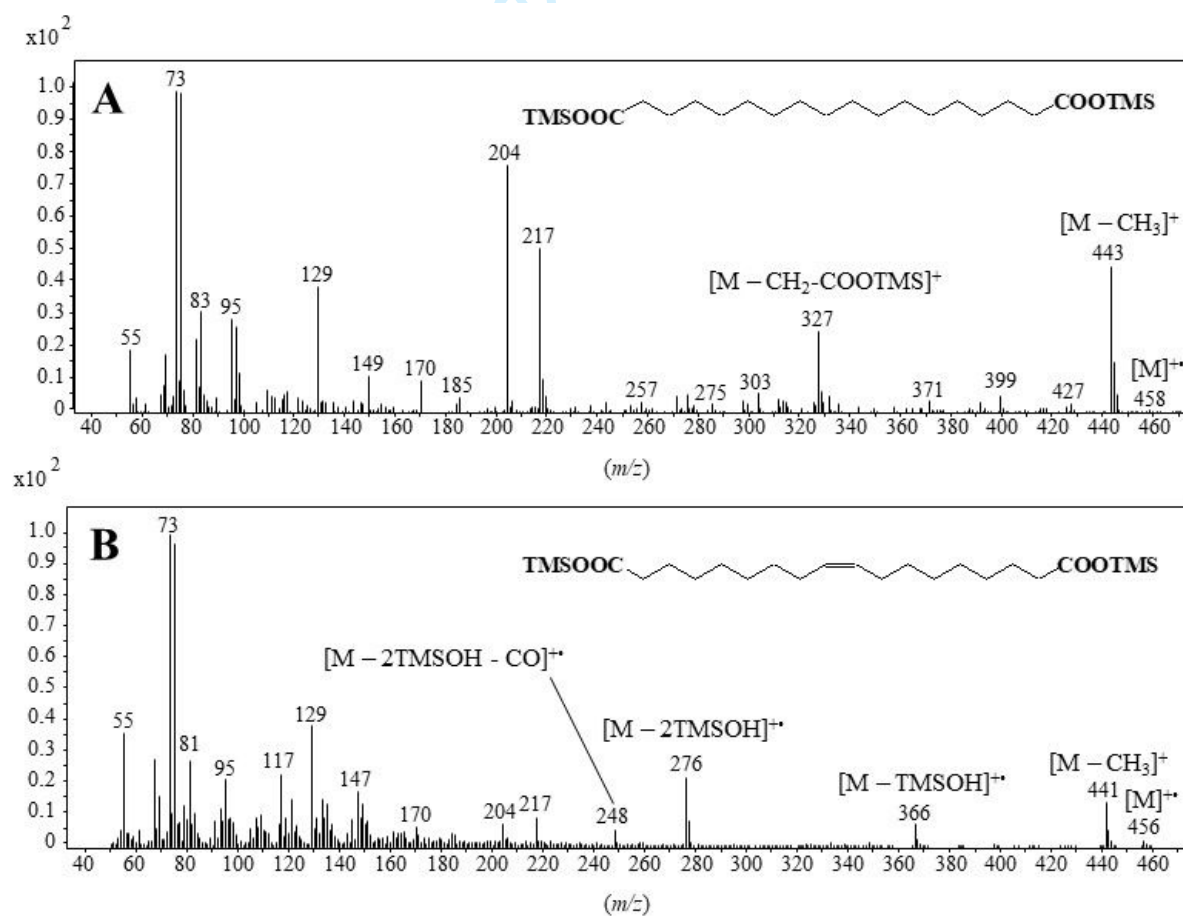
## CONCLUSIONS

EI-MS fragmentations of long-chain monounsaturated  $\alpha,\omega$ -dicarboxylic acids TMS derivatives exhibit specific fragment ions that can be very useful for the quantification in MRM mode of trace amounts of these compounds in environmental samples.

Dear Editor,

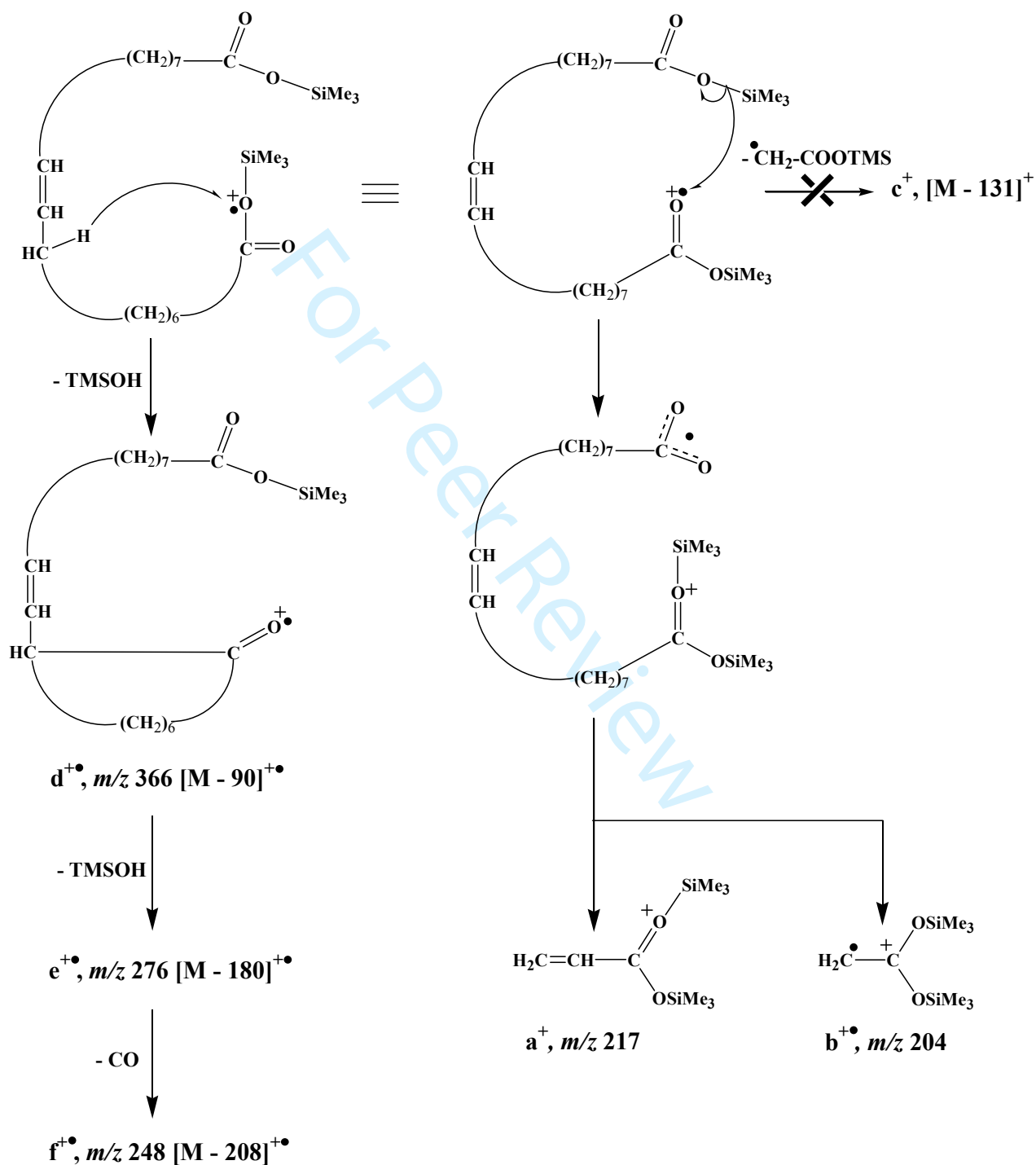
***Electron ionization mass fragmentation of monounsaturated long-chain  $\alpha,\omega$ -dicarboxylic acid trimethylsilyl derivatives***

Electron ionization (EI) mass spectral fragmentation of  $\alpha,\omega$ -dicarboxylic acid trimethylsilyl derivatives was previously investigated.<sup>1,2</sup> The mass spectra of these compounds exhibit intense fragment ions  $\mathbf{a}^+$ ,  $\mathbf{b}^{+\bullet}$  and  $\mathbf{c}^+$  at  $m/z$  217,  $m/z$  204 and  $M^{+\bullet} - 131$  ( $m/z$  327 in the case of octadecanedioic acid TMS derivative) (Fig. 1A). Fragment ions  $\mathbf{a}^+$  and  $\mathbf{b}^{+\bullet}$  are formed via an initial trimethylsilyl transfer between the two ester groups (Scheme 1),<sup>2</sup> which generally occurs through cyclic transition states,<sup>3</sup> and is thus favored in the case of long-chain diesters where intramolecular reaction is nearly strainless.<sup>4</sup> In the other hand, the formation of the fragment ion  $\mathbf{c}^+$  involves the loss of a radical  $\bullet\text{CH}_2\text{-COOTMS}$ .<sup>2</sup>



**FIGURE 1.** EI mass spectra of octadecanedioic acid (A) and octadec-9-enedioic (B) TMS derivatives

Octadec-9-enedioic acid trimethylsilyl derivative exhibits EI mass spectrum (Fig. 1B) quite distinct from this of its saturated counterpart (Fig. 1A), with weaker fragment ions  $\mathbf{a}^+$  and  $\mathbf{b}^{+\bullet}$ , lack of ion  $\mathbf{c}^+$  and the presence of intense additional ions at  $m/z$  366 ( $\mathbf{d}^{+\bullet}$ ),  $m/z$  276 ( $\mathbf{e}^{+\bullet}$ ) and  $m/z$  248 ( $\mathbf{f}^{+\bullet}$ ) corresponding to  $[\mathbf{M} - 90]^{+\bullet}$ ,  $[\mathbf{M} - 180]^{+\bullet}$  and  $[\mathbf{M} - 208]^{+\bullet}$ , respectively.



SCHEME 1

Measurements of accurate masses of ions  $\mathbf{d}^{+\bullet}$ ,  $\mathbf{e}^{+\bullet}$  and  $\mathbf{f}^{+\bullet}$  in TOF mass spectrum of octadec-9-enedioic TMS derivative revealed elemental compositions of  $\text{C}_{21}\text{H}_{38}\text{O}_3\text{Si}$  ( $m/z$  366.2579),  $\text{C}_{18}\text{H}_{28}\text{O}_2$  ( $m/z$  276.2086) and  $\text{C}_{17}\text{H}_{28}\text{O}$  ( $m/z$  248.2133), respectively. Moreover, low energy collision induced dissociation (CID/MS/MS) analyses with precursor ions at  $m/z$  366 ( $\mathbf{d}^{+\bullet}$ ) and  $m/z$  276 ( $\mathbf{e}^{+\bullet}$ ) allowed to demonstrate that ion  $\mathbf{e}^{+\bullet}$  is formed from ion  $\mathbf{d}^{+\bullet}$  and ion  $\mathbf{f}^{+\bullet}$  from ion  $\mathbf{e}^{+\bullet}$ . On the basis of these results, two subsequent losses of a neutral molecule of trimethylsilanol were proposed to explain the formation of ions  $\mathbf{d}^{+\bullet}$  and  $\mathbf{e}^{+\bullet}$  from the molecular ion (Scheme 1). These losses are initiated by the transfer of an allylic hydrogen atom to the ionized OTMS groups and result to the formation of cyclic ketonic structures (Scheme 1). A loss of a neutral molecule of CO, which is a characteristic of six and higher-membered cyclic ketones,<sup>5</sup> was proposed to explain the conversion of ion  $\mathbf{e}^{+\bullet}$  to ion  $\mathbf{f}^{+\bullet}$ . Due to the lack of allylic hydrogen atoms in saturated  $\alpha,\omega$ -dicarboxylic acid trimethylsilyl derivatives, ions  $\mathbf{d}^{+\bullet}$ ,  $\mathbf{e}^{+\bullet}$  and  $\mathbf{f}^{+\bullet}$  are totally lacking in EI mass spectra of these compounds (Fig. 1A). Mass-to-charge ratios and relative abundances of ions  $\mathbf{a}^+$ ,  $\mathbf{b}^{+\bullet}$ ,  $\mathbf{d}^{+\bullet}$ ,  $\mathbf{e}^{+\bullet}$  and  $\mathbf{f}^{+\bullet}$  in EI mass spectra of  $\text{C}_{14}$ - $\text{C}_{21}$  monounsaturated  $\alpha,\omega$ -dicarboxylic acid TMS derivatives are summarized in Table 1.

**Table 1.** Relative abundances of the fragment ions **a-f** in EI mass spectra of homologous monounsaturated  $\alpha,\omega$ -dicarboxylic acid di-TMS derivatives.

Diacids	$\mathbf{a}^+$	$\mathbf{b}^{+\bullet}$	$\mathbf{d}^{+\bullet}$ [M – TMSOH] $^{+\bullet}$	$\mathbf{e}^{+\bullet}$ [M – 2TMSOH] $^{+\bullet}$	$\mathbf{f}^{+\bullet}$ [M – 2TMSOH – CO] $^{+\bullet}$
$\text{C}_{14:1}$	217(5.3) <sup>a</sup>	204(6.4)	310(3.8)	220(6.7)	192(5.1)
$\text{C}_{15:1}$	217(7.0)	204(6.9)	324(3.1)	234(7.3)	206(5.6)
$\text{C}_{16:1}$	217(6.7)	204(7.0)	338(3.8)	248(15.8)	220(4.5)
$\text{C}_{17:1}$	217(6.3)	204(4.7)	352(4.0)	262(12.8)	234(3.6)
$\text{C}_{18:1}$	217(9.0)	204(8.4)	366(6.8)	276(23.7)	248(5.6)
$\text{C}_{19:1}$	217(6.7)	204(6.5)	380(4.6)	290(13.1)	262(3.7)
$\text{C}_{20:1}$	217(7.0)	204(6.9)	394(4.3)	304(11.6)	276(3.8)
$\text{C}_{21:1}$	217(5.8)	204(7.3)	408(4.0)	318(9.3)	290(2.5)

<sup>a</sup>  $m/z$ (relative abundance)

Long chain monounsaturated  $\alpha,\omega$ -dicarboxylic acids are important components of the cuticle and suberized cell walls of plants<sup>6,7</sup>. These compounds play a role in controlling solute and water transport across cell walls and provide a barrier against pathogens<sup>8</sup>. The transitions  $\mathbf{d}^{+\bullet} \rightarrow \mathbf{e}^{+\bullet}$ ,  $\mathbf{d}^{+\bullet} \rightarrow \mathbf{f}^{+\bullet}$  and  $\mathbf{e}^{+\bullet} \rightarrow \mathbf{f}^{+\bullet}$  should be very useful for the characterization in MRM mode of trace amounts of TMS derivatives of these compounds in environmental samples.

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