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Characterization of novel di- and tricarboxylic acids in fine tropical aerosols†

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Three unknown di- and tricarboxylic acids were characterized in the fine size fraction of aerosols which were collected during the wet season in the Amazon basin (Rondonia, Brazil). For the structural characterization of the methyl esters of these unknown compounds, mass spectrometry with electron ionization (EI) and tandem mass spectral techniques combined with gas chromatographic (GC) separation were employed. Fragment and parent ion spectra were recorded during elution of the GC peaks by linked scanning of the B and E sectors in combination with high-energy collision-induced dissociation. The fragmentation patterns of significant ions in the first-order EI spectra were also obtained for nonanedioic acid, which was examined as a model compound. The compounds were tentatively identified as 4-acetyloxyheptanedioic acid and *cis* and *trans* isomers of 5-hexene-1,1,6-tricarboxylic acid. Since there were indications of biomass burning during the aerosol sampling the di- and tricarboxylic acids characterized in the present work could be markers for biomass burning. Furthermore, the characterization of di- and tricarboxylic acids in the fine size fraction of atmospheric aerosols may be important for assessing the effects of organic aerosols in cloud formation.

KEYWORDS: dicarboxylic acids; tricarboxylic acids; gas chromatography/mass spectrometry; tandem mass spectrometry; collision-induced dissociation

INTRODUCTION

Aerosols play an important role in atmospheric chemistry, have an effect on human and animal health and affect climate. The climatic effect of aerosols is due to the fact that they physically influence the heat balance of the Earth, directly by reflecting sunlight and by absorbing and irradiating the infrared radiation of the Earth, in addition to indirectly by altering cloud properties and processes and possibly also by changing the heterogenic chemistry of greenhouse gases.[1] Atmospheric aerosols have a diameter varying between 1 nm and 10 μm with the largest part of their mass being in the region between 0.1 and 10 μm. They are formed by natural and anthropogenic processes which may show large regional and seasonal variations.[2,3] The production mechanisms are (1) direct injection of particles into the atmosphere, mainly by dispersion processes, resulting in the so-called 'primary' (or coarse, >1 μm) aerosols and (2) conversion of inorganic and organic gaseous precursors into secondary (or fine, <1 μm) particles. The characterization of the organic fraction of fine atmospheric aerosols, which has much less been studied than the inorganic fraction, is a topic of current interest in atmospheric chemistry because it may provide important information on sources (natural versus anthropogenic, primary versus secondary) and atmospheric processes (e.g. photochemical smog).[4]

In previous work we dealt with the characterization of organic compounds in the fine size fraction (<2 μm) of tropical atmospheric aerosols using detailed interpretation of mass spectral data obtained for methyl ester, methyl ester methoxime and trimethylsilyl (TMS) ester derivatives.[5] More specifically, two derivatives of glutaric acid, 3-isopropylpentanedioic and 3-acetylpentanedioic acid, another oxo homologue, 3-acetylhexanedioic acid, and a tricarboxylic acid, pentane-1,2,5-tricarboxylic acid, were tentatively identified. As the compounds were enriched in the fine size fraction of the tropical aerosol, suggesting that they were secondary organic aerosols constituents (i.e. formed by

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gas-to-particle conversion processes) and were also substantially enhanced in urban aerosol during a period of increased ozone concentrations, it has been argued that they may have significance as markers for atmospheric oxidation processes.

Dicarboxylic acids are ubiquitous organic aerosol constituents in the atmosphere and can be attributed to the formation by photochemical oxidation of anthropogenic hydrocarbons and biogenic compounds, to direct emission from combustion engines or to biomass combustion.[6–13] Atmospheric oxidation products (containing two or nine carbon atoms) include in addition to ω-dicarboxylic acids, keto mono- and dicarboxylic acids and α-dicarbonyls.[11,14] In contrast to dicarboxylic acids, little is known about the occurrence of tricarboxylic acids in atmospheric aerosols. To our knowledge, the tricarboxylic acids propane-1,2,3-tricarboxylic acid and pentane-1,2,5-tricarboxylic acid were first reported in our previous study on tropical and urban aerosols.[5]

In this study, we focused on the structural characterization of unknown di- and tricarboxylic acids, which were present in the fine size fraction of tropical aerosols collected during the wet season in the Amazon basin, Rondonia, Brazil, but were only minor components in that of tropical aerosol collected in another region of the Amazon basin, Balbina (130 km north of Manaus), also during the wet season. As there were indications of biomass burning (i.e. increased elemental carbon) for the aerosol sampling in Rondonia, the compounds identified in the present work could have significance as tracers for biomass burning processes. Furthermore, the presence of tricarboxylic acids may also contribute to the hygroscopic properties of the fine tropical aerosol, i.e. the capability of aerosols to act as cloud condensation nuclei[15] and also to influence the cloud formation processes by lowering the surface tension of droplets.[16]

For the chemical characterization of the compounds, gas chromatography/mass spectrometry (GC/MS) and tandem mass spectral techniques were employed. Fragment and parent ion spectra were recorded during elution of the GC peaks by linked scanning of the B and E sectors in combination with high-energy collision-induced dissociation (CID). Prior to the interpretation of the spectra of the unknown compounds, a known oxidative degradation product, nonanedioic acid (azelaic acid), was examined as a model dicarboxylic acid in attempt to establish some general fragmentation pathways of methylated organic acids with two or more carboxyl groups.

EXPERIMENTAL

Aerosol samples

Atmospheric aerosols were collected during a wet season LBA-EUSTACH campaign in Rondonia, Brazil, in spring 1999. A total filter[17] and a Hi-Vol dichotomous sampler[18] were used for sampling. The total filter sampler provided aerosol samples without size fractionation and was operated at a flow-rate of 100 l min^{-1}. The collection time per sample was 70 h. The open-faced samplers used a 47 mm diameter Whatman QM-A quartz fiber filter. The Hi-Vol sampler separated the aerosol into two size fractions, coarse and fine, with the separation between the two fractions at about 2–3 μm equivalent aerodynamic diameter (EAD). The flow-rates for the collection of the coarse and fine fractions were 30 and 270 l min^{-1}, respectively. The collection time per sample was typically 48 h. Pallflex quartz fiber filters (102 mm o.d.) were used to collect both size fractions.

All filters were subjected to analysis for organic carbon (OC) and elemental carbon (EC) by a thermal–optical transmission technique.[19]

Sample preparation

The filter samples were extracted three times, each time for 30 min with 20 ml of dichloromethane under ultrasonic agitation[20,21] in 25 ml Pyrex glass flasks with Teflon-lined stoppers.[22] The first extraction step was performed after acidification[23] to increase the extraction efficiency of acidic compounds. All glassware was deactivated with diazomethane prior to use. Before extraction, a mixture of two perdeuterated recovery standards (tetradecanoate, dotriacontane) was added to correct for losses during sample work-up.

The recovery, which was tested for azelaic acid, was found to be >95% and was assumed to be similar for di- and tricarboxylic acids.

For each filter, the combined dichloromethane extracts were concentrated to ~1 ml employing a rotary evaporator (533 hPa, 27 °C). Subsequently, the concentrated extract was filtered through a Teflon syringe filter (0.45 μm pore size) and completely dried under a stream of nitrogen. Finally, the dried sample was dissolved in dichloromethane (30 μl).

Derivatization techniques

The standard derivatization technique used for structural elucidation and quantification was methylation. Approximately 0.5 ml of a diethyl ether solution of diazomethane was added to the final extract. After 5 min, the solution was evaporated to dryness and the residue was dissolved in dichloromethane (30 μl).

To obtain additional information on unknown compounds, some of the final extracts were derivatized with *N,O*-bis (trimethylsilyl)trifluoroacetamide (BSTFA) and methoxyamine. Trimethylsilylation was performed by adding BSTFA–pyridine (1 : 1, v/v; 60 μl) and reacting for 1 h at room temperature. Derivatization with methoxylamine was performed by the addition of a solution of methoxylamine hydrochloride in pyridine (0.5%, 30 μl). The derivatization mixture was kept overnight. In both cases, solutions were dried and the residues were reconstituted into the original volume of solvent (30 μl).

Hydrogenation

The methylated extract was dissolved in methanol (0.5 ml) and platinum dioxide (10 mg) was added. The mixture was saturated with hydrogen for 30 min. After hydrogenation, the PtO_2 was removed from the solution by passing it through a silica column (5 cm × 0.5 cm i.d.) and the analytes were eluted with methanol (10 ml). The eluate was evaporated and reconstituted into the original volume of solvent (30 μl).

Extract analysis

The final extracts were subjected to qualitative and quantitative analysis using GC/MS and GC with flame ionization detection (FID).[5,22] First, an aliquot (1 μl) of the non-methylated extract was directly analyzed with co-injection of an internal standard (1-phenyldodecane). Subsequently, the remainder of the extract solution was methylated with diazomethane, the internal standard was added and the methylated extract was reinjected. Shifts of retention times observed after methylation were used for differentiating between acidic and non-acidic compounds in the sample.

Qualitative analyses were performed by GC/MS, using an HP 5890 gas chromatograph (Hewlett-Packard, Avondale, PA, USA) connected to a VG 70 SEQ hybrid mass spectrometer (Micromass, Manchester, UK). The gas chromatograph was equipped with a deactivated silica precolumn (2 m × 0.25 mm i.d.) and a low-bleed CP Sil 8CB capillary column (95% dimethyl, 5% phenyl polysiloxane; 0.25 μm film thickness, 30 m × 0.25 mm i.d.) (Chrompack, Middelburg, The Netherlands). A sample volume of 1.0 μl was injected into a split/splitless injector, operated in the splitless mode (splitless time: 60 s) at 250 °C. The carrier gas was helium at 50 kPa. The temperature program was started at 45 °C for 4 min, a steep gradient of 25 °C min^{-1} was used up to 100 °C, followed by 5 min at this temperature, then the temperature was increased to 315 °C at 5 °C min^{-1} and was held for 35 min. GC/MS analyses were performed in the electron ionization (EI) mode with an electron energy of 70 eV (trap current 50 μA) and the mass range m/z 50–550 was scanned at 1.5 s per decade. The accelerating voltage was 8 kV. The temperatures of the ion source and the transfer line were 230 and 275 °C, respectively.

GC/FID analyses of the methylated samples were used to obtain quantitative data on the total extractable and elutable mass of organic compounds (EEOC). The GC/FID mass determination was based on the response of known amounts of internal standard and recovery standards.[22] The GC/FID analyses were performed with an 8000 Top gas chromatograph (Carlo Erba, Milan, Italy). The analyses were performed with the same type of precolumn and chromatographic column and with the temperature program as used for GC/MS. The time at the initial GC temperature (45 °C) was shortened to 3 min to obtain the same retention times in both chromatographic systems. The same amount of sample was injected and the injector operated under the same conditions. Helium was employed as carrier gas at a pressure of 100 kPa. The flow-rates of the detector gases were 30 ml min^{-1} for H_2 and He and 300 ml min^{-1} for air. The detector temperature was 320 °C.

B/E linked scanning

B/E linked fragment ion spectra of unknown compounds were obtained with the same GC/MS system as used for EI spectra under the same GC and ion source conditions. The mass range m/z 10–300 was scanned at 1.5 s per decade. Fragment ion spectra were only recorded for selected chromatographic peaks corresponding to unknown products. Because the GC peaks were narrow (~5 s) B/E linked scan fragment ion spectra of only one ion per peak could be recorded during a chromatographic run. The fragmentation was increased by high-energy CID with helium. The pressure of helium in the first field-free region was adjusted until the polydimethylsiloxane ion at m/z 207 originating from the chromatographic stationary phase was decreased by 50%.

B^2/E linked parent ion spectra were obtained for confirmation of some fragmentation pathways, but the poor resolution of these spectra limited their usefulness.

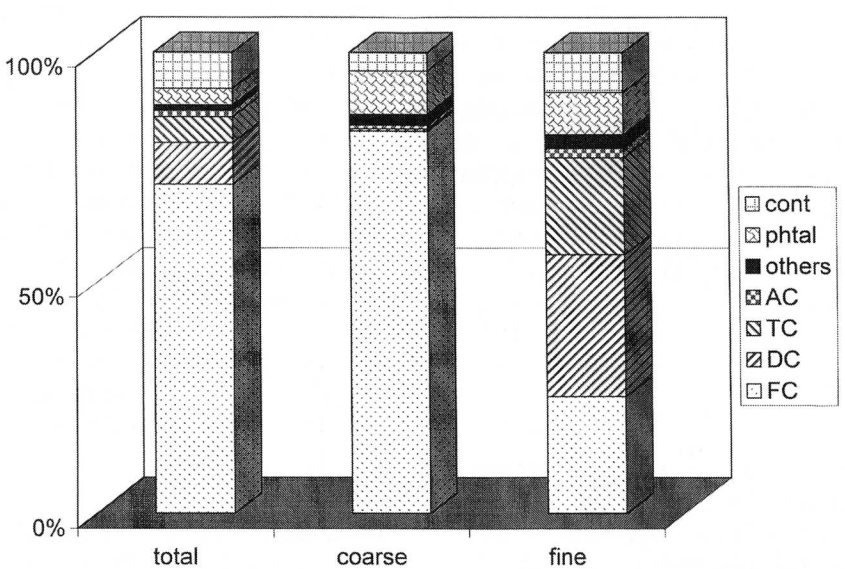

Figure 1. Percentage contributions of main compound classes in methylated extract relative to the identified extractable and elutable compounds (EEOC) for a selected total filter, and coarse and fine fractions of aerosol collected in Rondonia, Brazil. FC, fatty acids; DC, dicarboxylic acids; TC, tricarboxylic acids; AC, alkanes; phtal, phthalates; cont, contaminants. The last two groups probably originate from sampling and the analytical procedure, but they could also be present in sampled air. Taking this into account we preferred to include them in the calculation of the percentage contributions.

RESULTS AND DISCUSSION

Characterization and quantification of semi-volatile organic compounds were performed on methylated extracts of total filter, coarse and fine aerosol samples following procedures which have been described in detail in previous papers.[5,22] The percentage contributions of the main compound classes to the organic carbon mass are given in Fig. 1. The results show that there is a large difference between the coarse

Table 1. Atmospheric concentrations of oxidative degradation products and selected other aerosol parameters in total filter, coarse and fine aerosol samples from Rondonia, Brazil

Compound[a]	Units	Total filter (05.05·99)	Coarse (16.05·99)	Fine (16.05·99)
OC	$\mu g\ m^{-3}$	4.650	0.279	1.223
EC	$\mu g\ m^{-3}$	0.351	0.012	0.126
EEOC	$\mu g\ m^{-3}$	0.655	0.005	0.354
ODP	$ng\ m^{-3}$	32.8	n.d.[c]	30.3
DC9	$ng\ m^{-3}$	1.8	n.d.	0.9
DCpa[b]	$ng\ m^{-3}$	3.5	n.d.	4.5
DCpp[b]	$ng\ m^{-3}$	3.9	n.d.	2.2
DChxa[b] + TCpen[b]	$ng\ m^{-3}$	3.6	n.d.	4.7
1,1,2-TC2	$ng\ m^{-3}$	0.6	n.d.	0.8
1,1,3-TC3	$ng\ m^{-3}$	0.9	n.d.	0.5
1,2,3-TC3	$ng\ m^{-3}$	1.7	n.d.	0.8
1,2,4-TC4	$ng\ m^{-3}$	n.d.	n.d.	0.2
U_1	$ng\ m^{-3}$	2.6	n.d.	2.6
U_2	$ng\ m^{-3}$	2.2	n.d.	2.9
U_3	$ng\ m^{-3}$	2.1	n.d.	2.8

[a] EEOC refers to extractable and elutable organic compounds; ODP represents the sum of all oxidative degradation products; DC9, nonanedioic acid; DCpa, 3-acetylpentanedioic acid; DCpp, 3-isopropylpentanedioic acid; DChxa, 3-acetylhexanedioic acid; TCpen, pentane-1,2,5-tricarboxylic acid; 1,1,2-TC2, ethane-1,1,2-tricarboxylic acid; 1,1,3-TC3, propane-1,1,3-tricarboxylic acid; 1,2,3-TC3, propane-1,2,3-tricarboxylic acid; 1,2,4-TC4, butane-1,2,4-tricarboxylic acid.

[b] Compounds tentatively characterized in previous work.[5]

[c] Not detected.

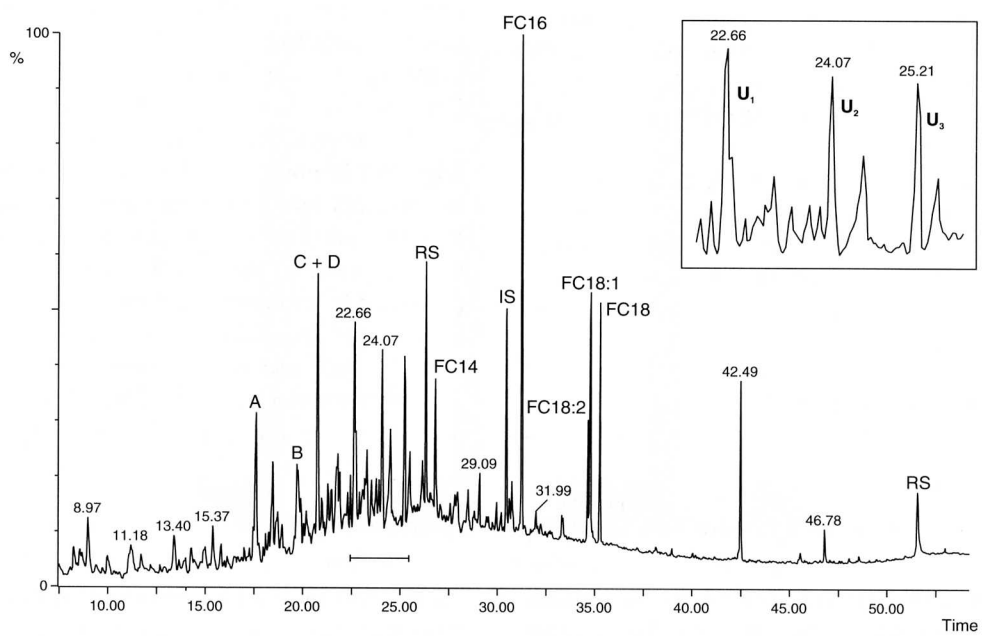

Figure 2. GC/MS TIC chromatogram obtained for a methylated extract of a fine aerosol sample collected in Rondonia, Brazil. Labeling: A, B, C/D, compounds identified in previous work; U_1, U_2, U_3, compounds identified in the present work; FC_X, fatty acids, where X represents the number of carbons; RS, recovery standard; IS, internal standard.

and fine aerosol fractions. A substantial part of the organic compounds in the fine aerosol fraction is made up by di- and tricarboxylic acids, some of which are believed to arise from fatty acids and/or terpenes by oxidative processes in the atmosphere.[23,24] These compounds are also found in the total filter samples which combine both the coarse and fine size fractions (Table 1).

Figure 2 illustrates a typical GC/MS total ion current (TIC) chromatogram obtained for a methylated extract of a fine aerosol fraction sample. The chromatogram contains several peaks which elute before palmitic acid between 16 and 26 min. These peaks could not be identified on the basis of a library search of known compounds but their mass spectra contained ions which pointed to dicarboxylic acids.

Peaks labeled A, B and C/D (Fig. 2) were characterized previously in tropical aerosols collected in Balbina, Brazil, during the wet season on the basis of a detailed interpretation of mass spectral data obtained for methyl ester, methyl ester methoxime and trimethylsilyl ester derivatives.[5] The peaks labeled U_1, U_2 and U_3 were only minor for aerosol samples collected in Balbina but appeared to be significant for samples collected in Rondonia, and were therefore, selected in the present study for structural characterization.

As none of the three unknown compounds reacted with methoxylamine after methylation, the presence of keto groups could be excluded. The EI spectra of the methyl esters of U_1, U_2 and U_3 are given in Figures 3(a), 4(a) and 5(a), respectively. The major ions at the highest m/z ratios in these spectra correspond to the $[M - OCH_3]^+$ ions. The spectrum of methylated U_1 shows an $[M - OCH_3]^+$ ion at m/z 215 indicating a molecular mass (M_r) of 218 for the underivatized dicarboxylic acid. A corresponding spectrum of the TMS ester derivative could not be obtained, possibly owing to the instability of the compound during trimethylsilylation.

The spectra of methylated U_2 and U_3 are similar and also show a characteristic $[M - OCH_3]^+$ ion at m/z 227 and an $[M - CH_3OH]^{+\bullet}$ ion at m/z 226 indicating an M_r of 216 for the underivatized tricarboxylic acids. Corresponding spectra of TMS ester derivatives reveal an $[M - CH_3]^+$ ion at m/z 417, confirming the M_r of 216.

In following steps an effort was made to interpret the spectra of the methyl esters of U_1, U_2 and U_3 in detail and, in order to facilitate the mass spectral interpretation, fragment and parent ion spectra were recorded for selected ions. Prior to interpreting the spectra of the unknown compounds we first examined a known oxidative degradation product, nonanedioic acid (azelaic acid), as a model dicarboxylic acid in order to establish some general fragmentation pathways of methylated organic acids with two or more carboxyl groups.

The first-order EI spectrum of methylated azelaic acid is illustrated in Fig. 6(a) and an overview of the fragmentation pathways is given in Scheme 1(a). The molecular ion (m/z 216) could not be detected. The ion at the highest m/z value is the $[M - OCH_3]^+$ ion (m/z 185), the fragment ion spectrum of which is given in Fig. 6(b). This spectrum shows very clearly that ions at m/z 152, 125, 97 and 83 result from fragmentation of the m/z 185 ion. The ions at m/z 143, 111, 87 and 74 which are observed in the first-order spectrum [Fig. 6(a)] must therefore be formed via other routes. Among these ions, the ions at m/z 74 and 87 are formed by hydrogen rearrangement processes, which have been studied in detail by McLafferty and co-workers for fatty acid methyl esters.[25] A plausible pathway resulting in the ion at m/z 143 corresponding to loss of a $CH_3OCOCH_2^\bullet$ part is proposed in Scheme 1(b). The loss of $CH_3OCOCH_2^\bullet$ from molecular ions of a series of homologous dicarboxylic acid dimethyl esters was examined by Schwarz,[26] who suggested a cyclic structure for the $[M - CH_3OCOCH_2^\bullet]^+$ ion. The m/z 143 ion can fragment further by sequential loss of CH_3OH and CO; the fragment ion spectrum of the m/z 143 ion indeed reveals ions at m/z 111 and 83. The parent ion (m/z 143) of the ion at m/z 111 was confirmed by a parent scan experiment.

The first-order EI spectra of methylated U_1 (Fig. 3(a)) shows an ion at m/z 186 corresponding to the loss of CH_3COOH and pointing to the presence of an acetyloxy group. The fragment ion spectra of the $[M - OCH_3]^+$ (m/z 215) and $[M - CH_3COOH]^{+\bullet}$ (m/z 186) ions are presented in Fig. 3(b) and (c). The mass spectral data obtained for methylated U_1 are summarized in Scheme 2(a). Based on the detailed interpretation of the mass spectral data discussed below, the structure of U_1 was tentatively assigned as 4-acetyloxyheptanedioic acid.

The loss of CH_3COOH involving the elimination of an acetyloxy group and leading to the ion at m/z 186 can occur before (thermal 1,2-elimination) or after ionization (Scheme 2(b) and (c)). The probable loss of CH_3COOH prior to ionization is consistent with the presence of an ion at m/z 113 (Fig. 3(c)) which can be formed by subsequent loss of a $CH_3OCOCH_2^\bullet$ moiety (Scheme 2(b)). The formation of an ion at m/z 186 by a combined loss of CO and $H^\bullet$ from the $[M - OCH_3]^+$ ion (m/z 215) indicates that there is more than one route leading to this ion (Fig. 3(b)). The latter route can also be reconciled with the location of the acetyloxy group in the 4-position and allows rationalization of the m/z 99 ion (Scheme 2(d)).

The ion at m/z 159 observed in the first-order spectrum (Fig. 3(a)) is not detected in the fragment ion spectra of the m/z 215 and 186 parent ions (Fig. 3(b) and (c)), and therefore must be formed directly from the molecular ion. It corresponds to the loss of a $CH_3OCOCH_2CH_2^\bullet$ moiety (87 u) and is consistent with the location of acetyloxy group in the 4-position (Scheme 2(e)). The subsequent combined loss of $CH_3O^\bullet$ and $H^\bullet$ represents one possible pathway of formation for the ion at m/z 127 which is the base peak in EI spectrum (Fig. 3(a)). Another pathway leading to a well-stabilized m/z 127 ion is proposed in Scheme 2(f) and is supported by fragment scan experiments on the ions at m/z 215 (Fig. 3(b)) and 155. Both proposed pathways are consistent with a parent scan experiment performed on the m/z 127 ion which reveals two parent ions at m/z 159 and 155.

As mentioned above, the spectra of U_2 and U_3 are similar (Figs 4(a) and 5(a)). Besides the characteristic ions $[M - OCH_3]^+$ (m/z 227) and $[M - CH_3OH]^{+\bullet}$ (m/z 226),

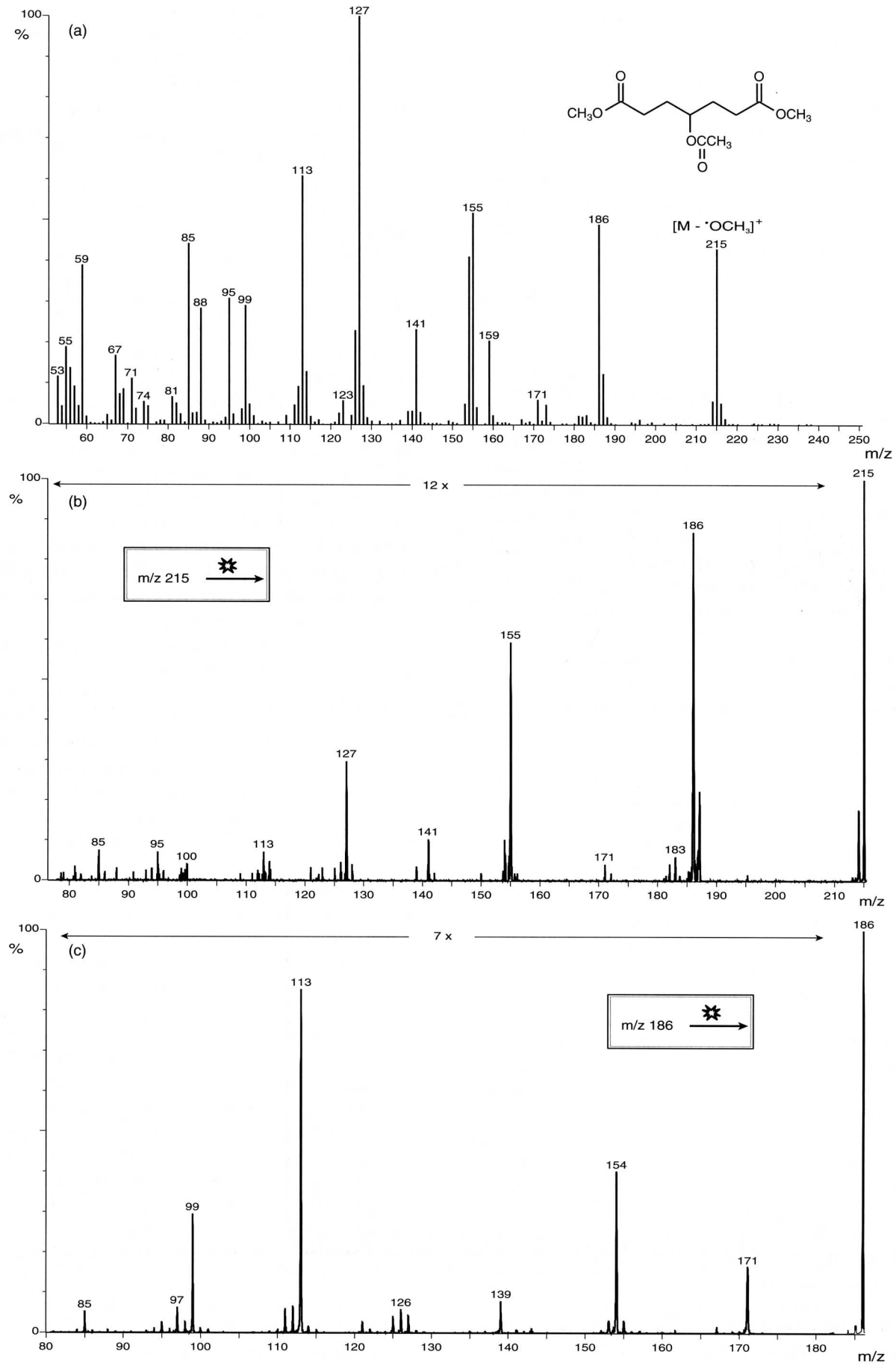

Figure 3. Unknown compound U_1 (tentative structure: 4-acetyloxyheptanedioic acid): (a) first-order EI spectrum; (b) fragment ion spectrum of the $[M - OCH_3]^+$ ion (*m/z* 215); (c) fragment ion spectrum of the $[M - CH_3COOH]^{+\bullet}$ ion (*m/z* 186).

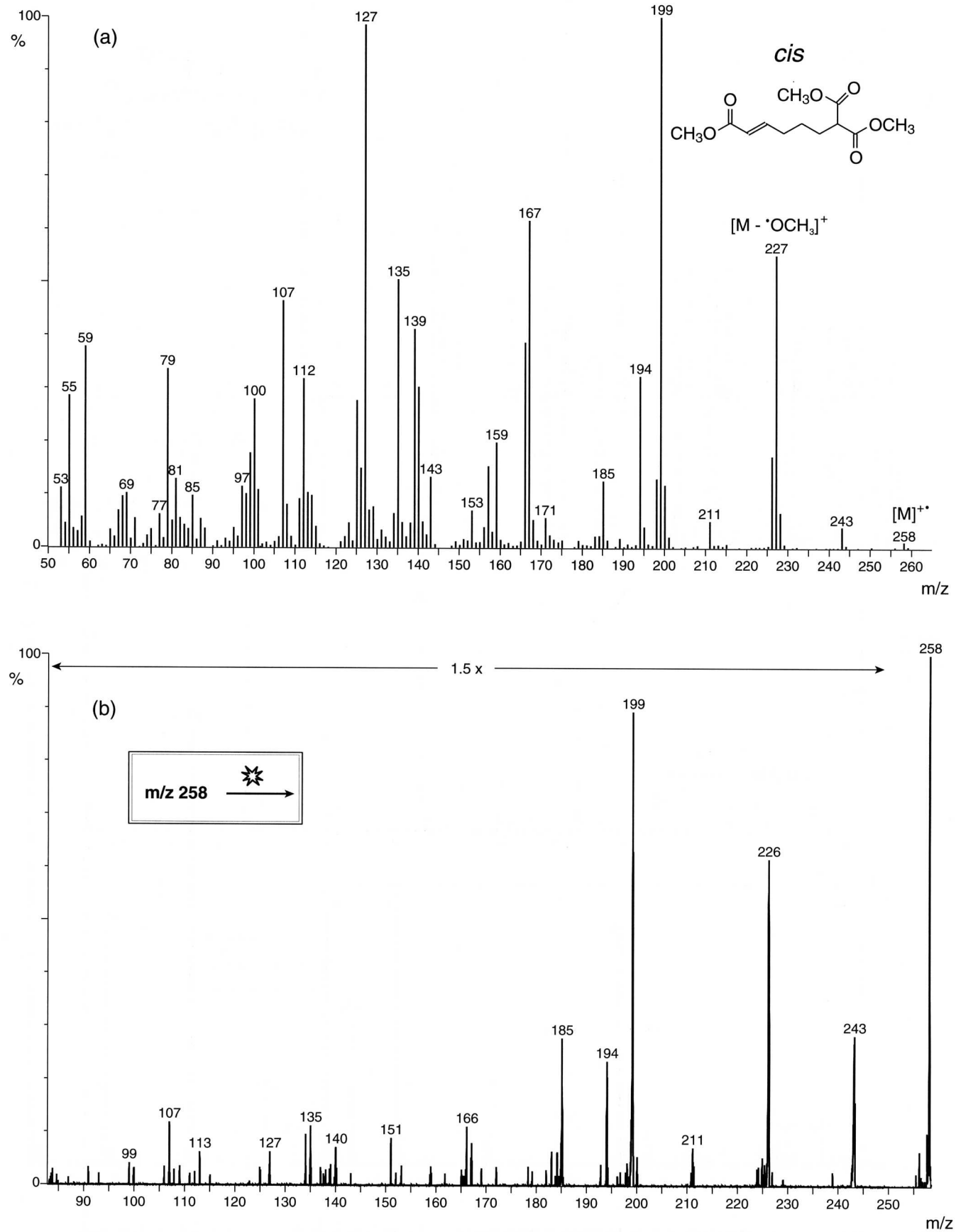

Figure 4. Unknown compound U_2 (tentative structure: *cis*-5-hexene-1,1,6-tricarboxylic acid): (a) first-order EI spectrum; (b) fragment ion spectrum of the $M^{+\bullet}$ ion (*m/z* 258).

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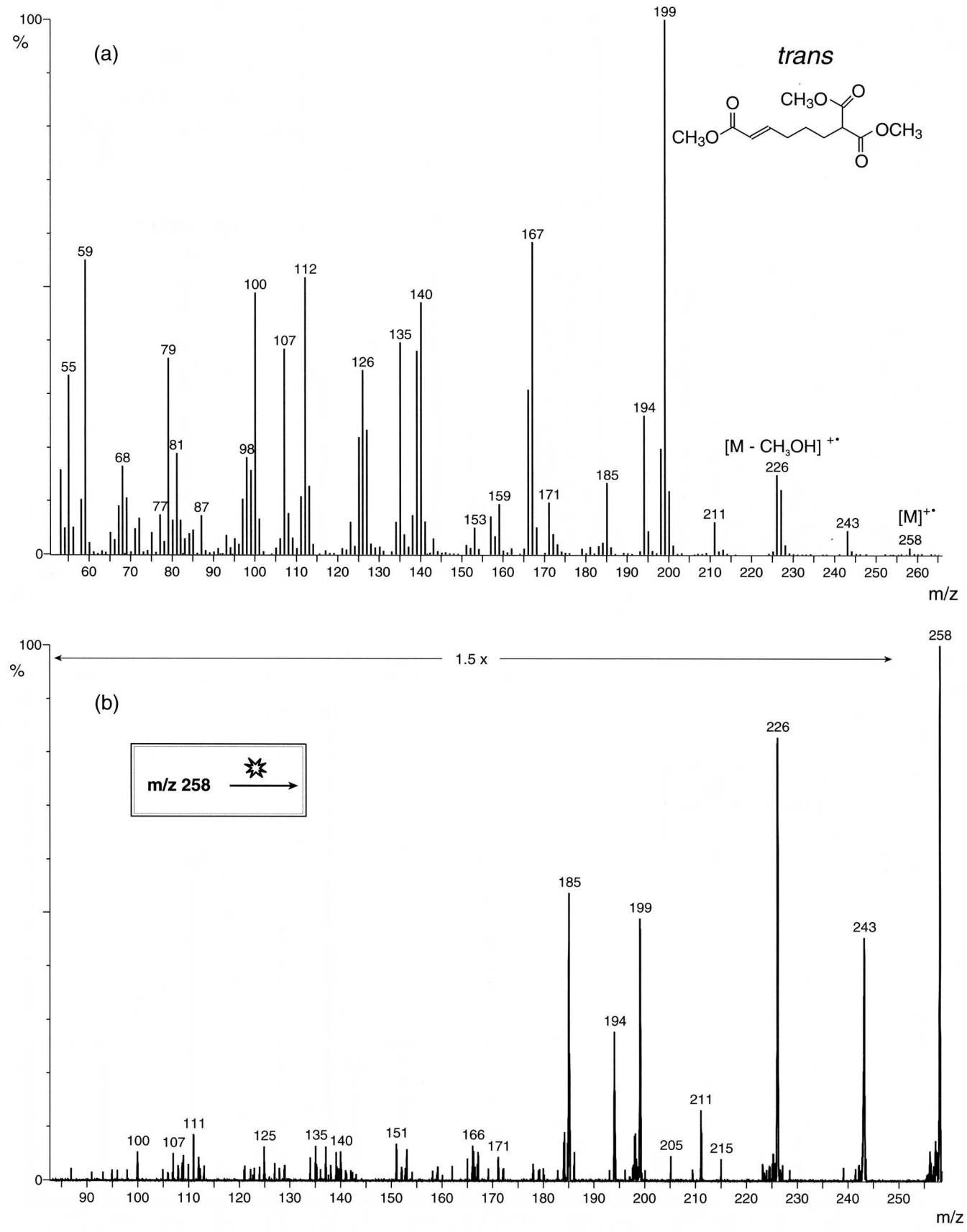

Figure 5. Unknown compound U_3 (tentative structure: *trans*-5-hexene-1,1,6-tricarboxylic acid): (a) first-order EI spectrum; (b) fragment ion spectrum of the $M^{+\bullet}$ ion (*m/z* 258).

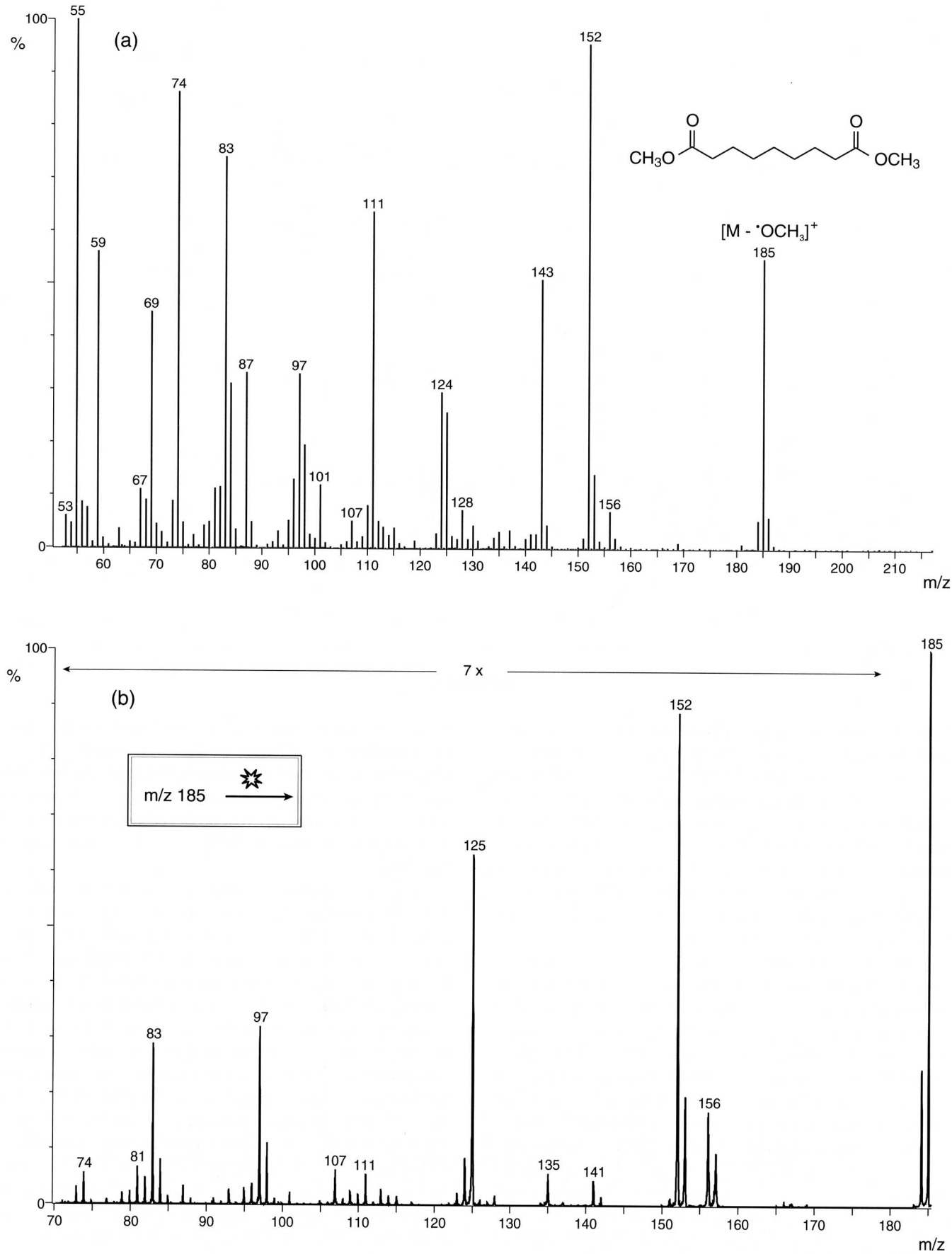

Figure 6. Model compound (azelaic acid): (a) first-order EI spectrum; (b) fragment ion spectrum of the $[M - OCH_3]^+$ ion (*m/z* 185).

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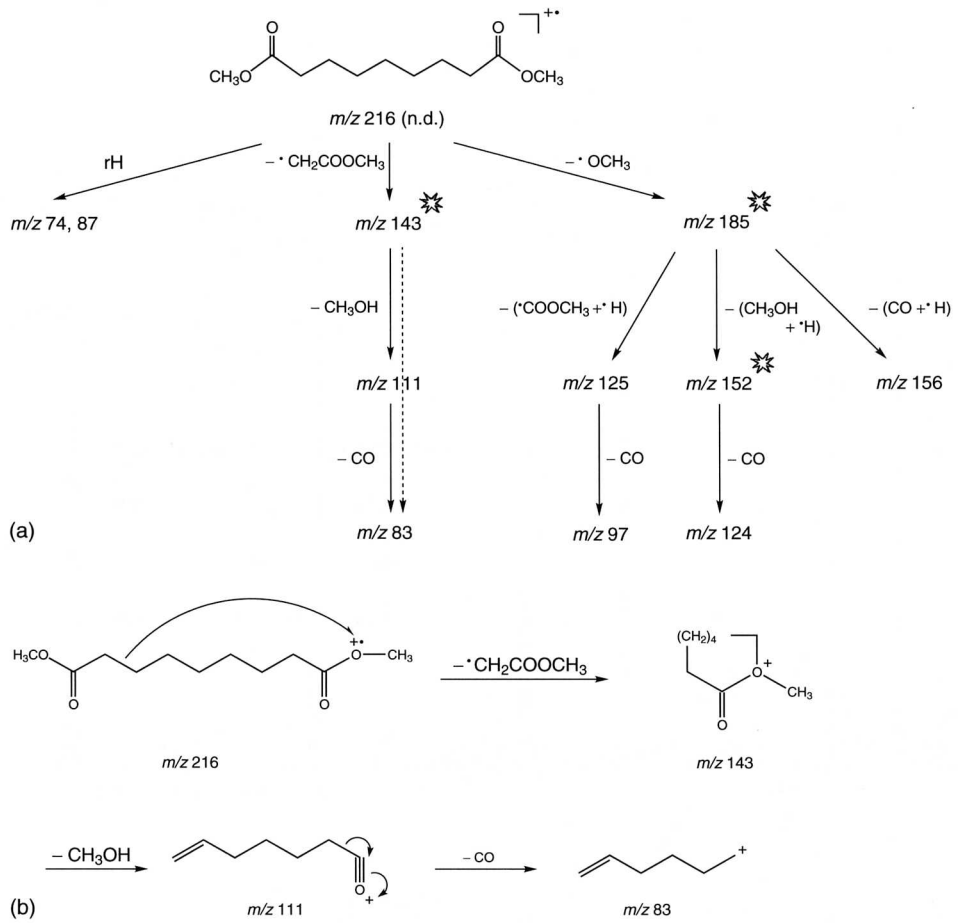
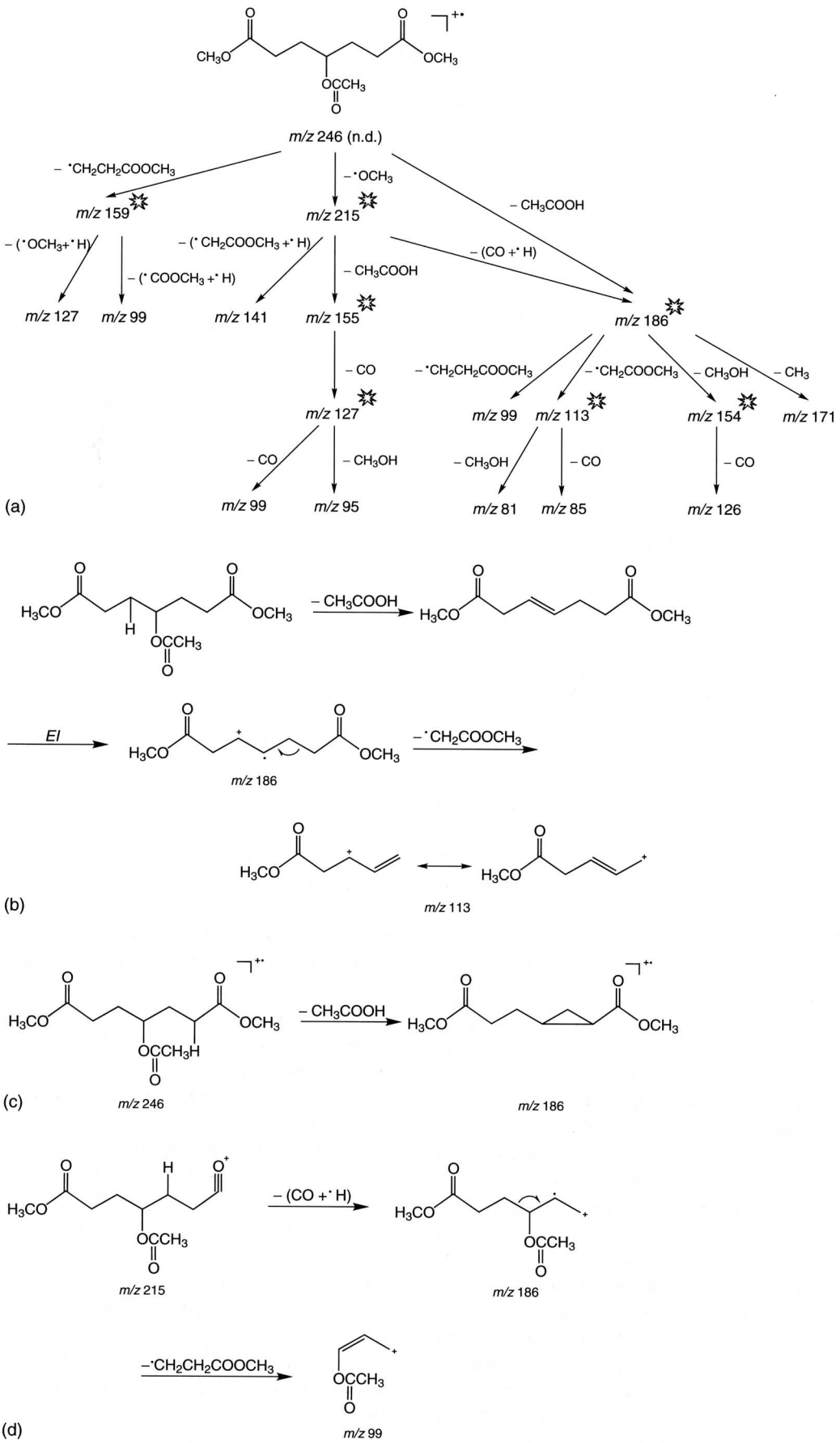


Scheme 1

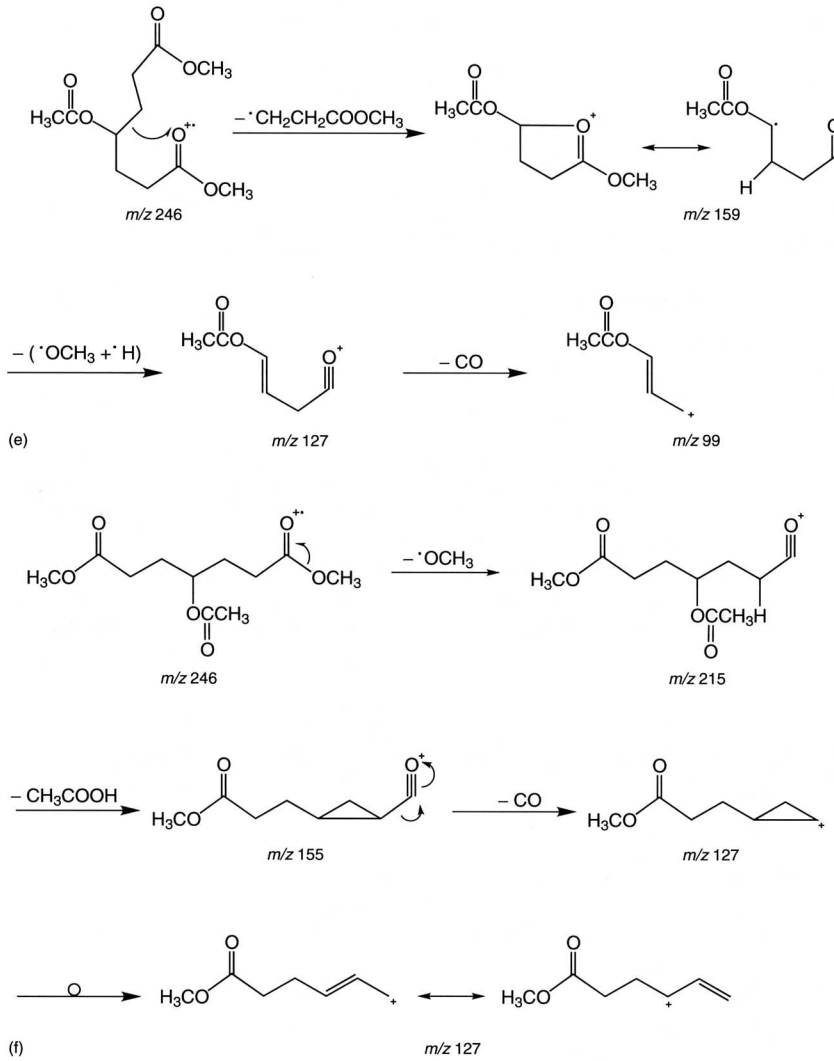
both first-order EI spectra show ions with low relative abundance at m/z 258 and 243 corresponding to the $M^{+\bullet}$ and $[M - 15]^+$ ion, respectively. The most abundant ion at m/z 199 is due to the loss of one methylated carboxyl group. The formation of the ions at m/z 243, 226, 199 and 185 directly from $M^{+\bullet}$ (m/z 258) was confirmed by a fragment ion experiment (Figs 4(b) and 5(b)). An overview of the fragmentations of methylated U_2 and U_3 is given in Scheme 3(a). U_2 and U_3 were tentatively identified as *cis*- and *trans*-5-hexene-1,1,6-tricarboxylic acid.

The first-order (Figs 4(a) and 5(a)) and fragment ion spectra (Figs 4(b) and 5(b)) only reveal differences in the relative abundances of some ions which can be regarded as characteristic of *cis*/*trans* isomeric compounds. Comparison of the first-order spectra shows that the $[M - OCH_3]^+/[M - CH_3OH]^{+\bullet}$ ratio is significantly different between methylated U_2 and U_3. In addition, the ion at m/z 127 is a major ion in the first order spectrum of methylated U_2 but is much less abundant in that of methylated U_3. Furthermore, it is worth noting that the ion at m/z 127 could only be detected with a very low relative abundance in the fragment ion spectra. A parent ion experiment on the m/z 127 ion indicated that the precursor was the ion at m/z 159 (not shown). A plausible pathway leading to the formation of the ion at m/z 127 for the methylated *cis* isomer is given in Scheme 3(b). It is reasonable to propose that the loss of the $CH_3OCOCH{=}CHCH_2^\bullet$ part (99 u) will be influenced by *cis*/*trans* isomerism of the double bond. The fragment ion scan of the m/z 127 ion (not shown) revealed the loss of CO, which is consistent with the proposed ion structure. The parent ion scan experiment on the ion at m/z 159 was not successful (no parent ion was observed), probably because the loss of $CH_3OCOCH{=}CHCH_2^\bullet$ corresponds to a very fast reaction.

A rationalization for the ion at m/z 126, which is relatively more abundant in the *trans* than in the *cis* isomer, is given in Scheme 3(c). Again, it is reasonable to propose that *cis*/*trans* isomerism of the double bond will affect hydrogen rearrangement from the 4-position to the carboxyl substituent. Following hydrogen rearrangement, charge-driven reactions result in the formation of the m/z 126 ion. It also may be argued that this reaction competes with the loss of a $CH_3O^\bullet$ group providing an explanation for the lower relative abundance of the $[M - OCH_3]^+$ ion (m/z 227) in the *trans* isomer compared with the *cis* isomer. The double bond is probably located at the 5-position, in conjugation with the carbonyl group. This is consistent with hydrogenation experiments which failed, indicating that the double bond could not be at any other position on the chain. The assignment of U_2 and U_3 as *cis* and *trans* isomers, respectively, also fitted with the general chromatographic behavior of *cis*/*trans* isomers of monounsaturated carboxylic acids on the used column for which *cis* isomers elute before corresponding *trans* isomers.



Scheme 2



Scheme 2. (*continued*).

CONCLUSIONS

The three unknown products which were enriched in the fine size fraction of tropical aerosols were characterized using detailed interpretation of EI mass spectral data obtained for methyl ester derivatives. The compounds were tentatively identified as 4-acetyloxyheptanedioic acid and *cis* and *trans* isomers of 5-hexene-1,1,6-tricarboxylic acid.

The proposed fragmentation pathways were supported by fragment and parent ion scan experiments which were performed during elution of the chromatographic peaks by linked scanning of the B and E analyzers and high-energy CID.

Since the identified products were detected in aerosols for which another pyrogenic marker, i.e. elemental carbon, was increased, they may possibly have significance as markers for biomass burning. In future work we will evaluate how the concentrations of the latter compounds correlate with those of other pyrogenic markers, such as elemental carbon and levoglucosan.[27] Structurally related di- and tricarboxylic acids have been characterized in previous work for aerosols collected during the wet season for which there was no indication of biomass burning. The latter compounds were attributed to atmospheric oxidation of natural biogenic hydrocarbons but their precursors could not be pinpointed.[5] Dicarboxylic acids originating from ozone oxidation of monoterpenes such as α- and β-pinene have been reported in recent studies[24,28–30] but the corresponding oxidation products could not be detected in the present study. To our knowledge, pinonic acid due to ozone oxidation of α-pinene has only been reported for aerosols formed above coniferous forests.[31]

The presence of di- and tricarboxylic acids in the fine size fraction of tropical aerosols may, in view of their hygroscopic properties, be important for assessing the effects of organic aerosols in cloud formation.

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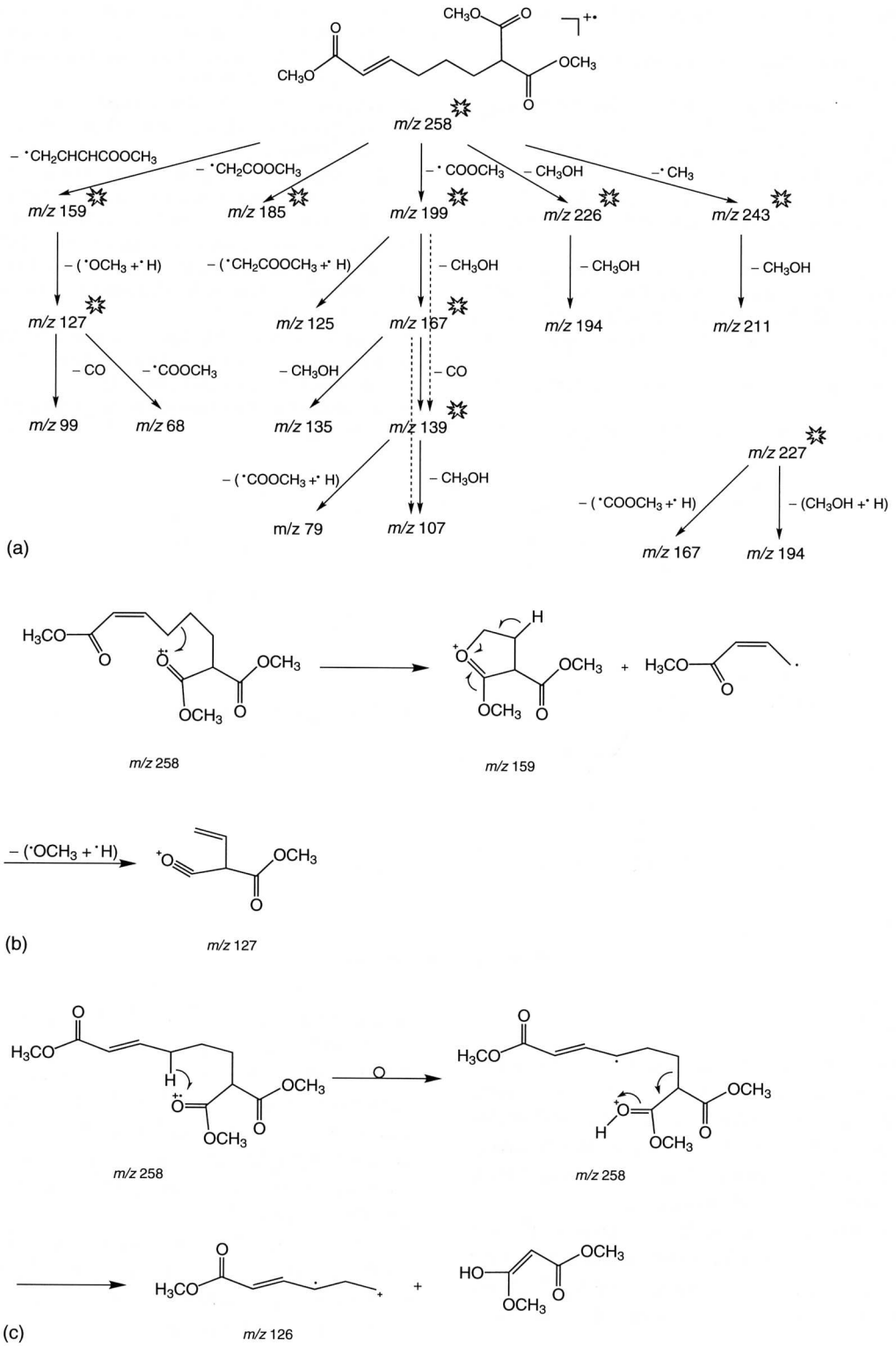

Scheme 3

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