

Organic Hydroxy Acids as Highly Oxygenated Molecular (HOM) Tracers for Aged Isoprene Aerosol

Mohammed Jaoui,^{*,†} Rafal Szmigielski,^{*,‡} Klara Nestorowicz,[‡] Agata Kolodziejczyk,[‡] Kumar Sarang,[‡] Krzysztof J. Rudzinski,[‡] Anna Konopka,[§] Ewa Bulska,[§] Michael Lewandowski,[†] and Tadeusz E. Kleindienst[†]

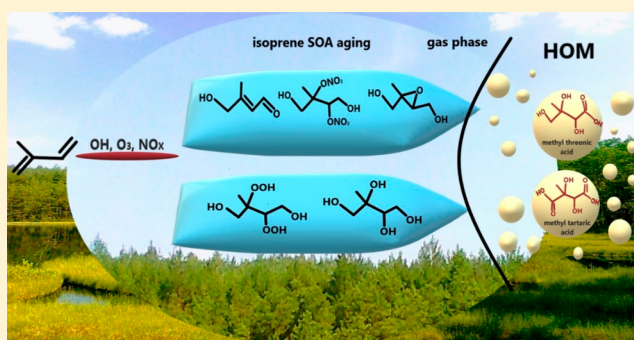
[†]National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, United States

[‡]Environmental Chemistry Group, Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

[§]University of Warsaw, Faculty of Chemistry, Biological and Chemical Research Centre, Żwirki i Wigury 101, 02-089 Warsaw, Poland

S Supporting Information

ABSTRACT: Highly oxygenated molecules (HOMs) are a class of compounds associated with secondary organic aerosols exhibiting high oxygen to carbon (O:C) ratios and often originating from the oxidation of biogenic compounds. Here, the photooxidation and ozonolysis of isoprene were examined under a range of conditions to identify HOM tracers for aged isoprene aerosol. The HOM tracers were identified as silylated derivatives by gas chromatography–mass spectrometry and by detecting their parent compounds by liquid chromatography–high resolution mass spectrometry. In addition to the previously observed methyltetrols and 2-methylglyceric acid, seven tracer compounds were identified, including 2-methyltartaric acid (MTtA), 2-methylerythronic acid (2MeTrA), 3-methylerythronic acid (3MeTrA), 2-methylthreonic acid (2MTrA), 3-methylthreonic acid (3MTrA), *erythro*-methyltartaric acid (e-MTA), and *threo*-methyltartaric acid (t-MTA). The molecular structures were confirmed with authentic standards synthesized in the laboratory. The presence of some of these HOMs in the gas and particle phases simultaneously provides evidence of their gas/particle partitioning. To determine the contributions of aged isoprene products to ambient aerosols, we analyzed ambient PM_{2.5} samples collected in the southeastern United States in summer 2003 and at two European monitoring stations located in Zielonka and Godów (Poland). Our findings show that methyltartaric acids (MTA) and 2- and 3-methylthreonic acids (and their stereoisomers) are representative of aged isoprene aerosol because they occur both in the laboratory chamber aerosol obtained and in ambient PM_{2.5}. On the basis of gas chromatography–mass spectrometry (GC-MS) analysis, their concentrations were found to range from 0.04 ng for 3-methylthreonic acid to 6.3 ng m⁻³ for methyltartaric acid at the southeast site in Duke Forest, NC, USA.



1. INTRODUCTION

Organic aerosols (OAs) make up a significant fraction of PM_{2.5}; that is, particles having an aerodynamic diameter less than 2.5 μm .^{1,2} The origin of OAs is from fossil fuel combustion, biomass burning, and other primary sources, as well as from the oxidation of volatile and semivolatile organic compounds in the atmosphere. Secondary organic aerosols (SOAs), which can contribute significantly to ambient PM_{2.5}, are also formed from the heterogeneous oxidation of compounds in the particle phase.³ Exposure to PM_{2.5} is known to be a detriment to human health, to degrade visibility, and to influence the energy budget of the earth.^{4–6} The oxidation products of isoprene forming an organic aerosol represent a major input to the global SOA burden.^{7,8}

Isoprene has been the subject of extensive studies in aerosol chemistry ever since 2-methylthreitol (2MTr) and 2-methylerythritol (2MeT; collectively methyltetrols, MTs) were discovered to arise from the oxidation of isoprene in the Amazon rainforest.^{9,10} While Claeys et al.⁹ identified the compounds, Edney et al.¹⁰ provided direct evidence for their formation from laboratory irradiations of isoprene in the presence of oxides of nitrogen. Since that time, additional isoprene particle phase products, including 2-methylglyceric acid (2MGA), C₅-alkene triols, C₄–C₅-organosulfates/organonitrates, and dihydroperoxydiols, have been detected in urban,

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rural, and remote environments.^{11–18} Polar organic compounds upon silylation result in reduced polarity, enhanced volatility, and increased thermal stability and enable a GC-MS analysis for a number of involatile or too unstable compounds. However, appropriate caution should be taken, for example, with desulfation reactions associated with primary organosulfates, and corrections might be warranted when methyltetros are analyzed.^{19–23}

It is now thought that much, if not the majority, of SOAs in PM_{2.5} results from organics that have undergone several generations of atmospheric oxidation. Multiple insights^{24–26} have illuminated the nature of this oxidized carbon, referred to as “aged carbon”, giving rise to highly oxygenated molecules (HOMs).²⁷ For example, Sato et al.²⁸ reported the presence of such species following ozonolysis reactions of β -pinene producing gas and particle products which in turn react with hydroxyl radicals (OH). In contrast, Ehn et al.,²⁹ Kristensen et al.,³⁰ and Jokinen et al.³¹ have suggested that highly oxidized organic compounds are formed at early stages in the oxidation of monoterpenes. Rissanen et al.³² have proposed a mechanistic description of such extremely low volatility organic compounds from the ozonolysis of cyclohexene. Several recent studies of isoprene oxidation have shown the prevalence of low-volatility highly oxidized molecules in SOAs.^{33,34} Considerable effort is now underway to characterize organic species associated with biogenic SOA aging to incorporate it into atmospheric models.^{25,26,35–37} However, there are few metrics which can be used to adequately assess the degree of oxidation of such HOMs in air quality model predictions.

Here, we report on the formation of such particulate carbon compounds (having oxygen to carbon mass ratios greater than unity; O:C \geq 1) from the laboratory oxidation of isoprene (ISO) by O₃ and OH radicals. These experiments have been conducted under a range of nitrogen oxide and acidic sulfate aerosol concentrations. Analytical methods coupling gas chromatography to mass spectrometry (GC-MS) and liquid chromatography to high-resolution Orbitrap mass spectrometry (LC-HR Orbitrap MS) have led to the identification of a novel class of tracer compounds from samples obtained from controlled chamber experiments. Syntheses of reference compounds in our laboratory allowed for definitive structural identifications of the markers. Moreover, PM_{2.5} samples from urban, rural, and remote areas from Europe and the United States have indicated that this novel class of compounds (hydroxy carboxylic acids) is found in ambient samples at levels near or exceeding that of methyltetros.^{9,10}

2. EXPERIMENTAL METHODS

All chemicals were purchased at the highest purity available from Aldrich Chemical Co. (Milwaukee, WI) and were used without further purification. Solvents used in GC-MS (GC² quality) were from Burdick and Jackson (Muskegon, MI). For LC-MS, water (resistivity 18.2 M Ω cm) was purified with a Milli-Q Advantage system from Merck (Poland) and methanol (ChromaSolv-Grade) was purchased from Sigma-Aldrich (Poland). The synthesis procedures of 2-methylthreonic acid, 3-methylthreonic acid, and methyltartaric acid involved generating trihydroxymethyl ester salts followed by a dihydroxylation reaction to afford reference products. Detailed procedures for the synthesis are provided in [section S1](#) in the Supporting Information.

The experiments were conducted in a 14.5 m³ fixed-volume chamber with walls having a 40 μ m Teflon coating. The

standard photolytic system produced radiation in the actinic region of the spectrum (300–400 nm). For irradiations in the presence of nitrogen oxides (NO_x), OH was produced by the conventional chain-propagating mechanism where NO oxidizes ozone and peroxy radicals formed in the system. In other experiments, OH was generated in the absence of NO_x by photolyzing H₂O₂, where additional UV sunlamps increased the radiation by 280–320 nm. Additional details on the chamber operation, procedures, and instruments have been reported in our previous papers.^{38,39} Chamber isoprene concentrations were measured by GC/FID (Hewlett-Packard, Palo Alto, CA; Model 5890). Ozone was measured with a Bendix ozone monitor (Model 8002, Lewisburg, WV). NO and NO_x were monitored with a TECO oxides of nitrogen analyzer (Model 42C, Franklin, MA).

Particle samples from the chamber were collected onto 47 mm glass fiber filters at 16.7 L min^{−1} for 1 h just after adding all the reactants in the static (batch) mode and 24 h in the dynamic (flow) mode. They were sonicated for 1 h in 5 mL of methanol. Prior to extraction, known masses of *cis*-ketopinic acid (KPA) and *d*₅₀-tetracosane (TCS) were spiked on each filter as internal/recovery standards. The extraction efficiency was determined for 3-methylthreonic acid (84.7 (\pm 4.2)%), and methyltartaric acid (87.5 (\pm 4.1)%) using HPLC-Q-ToF MS. Similar values were reported previously on the basis of similar organic compounds.^{38,39} Each extract was evaporated to dryness under a gentle stream of N₂ at room temperature and then derivatized with 200 μ L of BSTFA (N,O-bis-(trimethylsilyl)trifluoroacetamide: 1% trimethylchlorosilane) and 100 μ L of pyridine at 70 °C for 1 h.^{38,41} The silylated extracts were analyzed for organic compounds, and only targeted species are reported in this study. The organic compounds were analyzed by GC-MS, with details being given in [section 3](#) in the Supporting Information.

UHPLC-ESI-MS/MS analysis was performed for organic acids using a Dionex UltiMate 3000 RSLC system (Thermo Fisher Scientific) coupled to an Orbitrap Fusion Tribrid mass spectrometer (Thermo Fisher Scientific) equipped with a heated electrospray ionization source (HESI). UHPLC-ESI-MS/MS was used as an independent method to confirm the identity of the targeted isoprene HOM compounds measured by GC-MS. Compounds were separated on an Acquity UPLC HSS T3 column, 2.1 mm i.d. \times 100 mm, particle size 1.8 μ m, pore size 100 Å (Waters), at 40 °C. Water with 10 mM ammonium formate and methanol with 10 mM ammonium formate were used as solvents A and B, respectively. Samples were loaded directly onto an analytical column at a flow rate of 0.3 mL min^{−1} of 100% solvent A. The injection volumes were 1 and 20 μ L for the survey scans and the MS/MS spectra scans, respectively. Compounds were eluted from the column at a flow rate of 0.3 mL min^{−1} with the following linear gradient: 0 min, 100% A; 3 min, 100% A; 6 min, 100% B; 9 min, 100% B; 12 min, 100% A. The eluted compounds were ionized in the negative ion mode with a capillary voltage of 2.5 kV in an HESI source. The ion source working parameters optimized on the total ion current (TIC) values were as follows: sheath gas flow 35 L min^{−1}, auxiliary gas flow 10 L min^{−1}, ion transfer tube temperature 325 °C, and vaporizer temperature 275 °C. Nitrogen was used as the sheath and auxiliary gas. Survey scans were recorded in the Orbitrap mass analyzer at a resolving power of 60000 in the *m/z* range of 50–300. From each survey scan the most abundant singly charged ions were fragmented by higher energy collision-induced

Table 1. Initial and Input Conditions for Isoprene Experiments^a

experiment	ISO (ppm)	NO (ppm)	O ₃ (ppm)	H ₂ O ₂ (ppm)	acidic seed (mg L ⁻¹)	hexane (ppm)	RH (%)	T (°C)	residence time (h)
1 ^b (SE)	0.68		0.990				<3	19	
2 ^b (SE)	0.68		1.030			350	<3	20	
3 ^c (SE)	3.65	0.427					30	20	
4 ^c (DE)	3.08	0.300					30	29	4.08
5 ^c (DE)	3.14	0.300					30	29	4.08
6 (DE)	2.20			4.7			<3	25	4.60
7 (SE)	2.78			5.8			<5	21	
8 (DE) ^{d,g}	1.40	0.296			60		44	27	3.80
8 (DE) ^{d,f}	1.64	0.347					49	28	3.86

^aIn experiments without NO_x, H₂O₂ served as the OH precursor. Abbreviations: DE, dynamic mode; SE, static mode (initial concentrations are given). ^bDetailed information about some experiments used in this study can be found in Kleindienst et al.⁴⁵ ^cDetailed information about some experiments used in this study can be found in Surratt et al.⁴⁶ ^dDetailed information about some experiments used in this study can be found in Lewandowski et al.⁴⁷ and Nestorowicz et al.⁴³ ^eDetailed information about some experiments used in this study can be found in Jaoui et al.⁴² Experiment 8 was conducted in two stages. ^fAtomizing solution: (NH₄)₂SO₄ at 0.5 mg L⁻¹. ^gatomizing solution: (NH₄)₂SO₄ at 41 mg L⁻¹ and H₂SO₄ at 60 mg L⁻¹. Chambers often exhibit a NO_x background (<1 ppb) that is present even when NO_x is not deliberately added.

dissociation (HCD). The cycle time was 3 s. The product ions were analyzed in the Orbitrap analyzer at a resolving power of 15000. After fragmentation, the masses were excluded for 30 s from further fragmentation. Collision energy values were optimized to obtain good fragmentation of the compounds studied. Survey scans and MS/MS spectra were evaluated manually using Xcalibur 3.0 (Thermo Fisher Scientific). Blanks and background samples were extracted and analyzed identically as the field/chamber samples and gave negligible signals of the targeted SOA compounds.

Ambient PM_{2.5} samples were collected from several sites in Europe and the United States: two regional background monitoring stations located in Zielonka and Godów (Poland) and one site at the Duke University Research Forest (DF; Blackwood Division). Extended analysis of field samples is reported in the paper associated with the HOM formation mechanism, time series, and implication to ambient PM_{2.5}.⁴² Detailed descriptions of the field sites and sampling procedures have been reported previously^{43,44} and are described in section S2 in the Supporting Information.

Initial conditions for a subset of experiments, representative of a large group conducted during the past 15 years in our laboratory, are given in Table 1. Two sets of experiments were conducted. In the first set, four experiments (1–3 and 7) were carried out with the chamber operated in a batch mode. In the second set, four experiments (4–6 and 8) were conducted with the chamber operated in a flow mode with a residence time of 4 h. A further description of each experiment is reported in section S3 in the Supporting Information.

3. RESULTS AND DISCUSSION

While the putative isoprene HOM tracers can be found in field samples, they are most readily isolated and identified by laboratory experiments. Here, the conditions of individual experiments represent the types of atmospheric reactions likely to occur. The tracers have been identified using the method of Jaoui et al.^{38,41} The GC-MS (methane CI) extracted-ion chromatograms in Figure 1 use the selected ions (*m/z* 165, 321, 335, 409, 423, and 437) to best illustrate the presence of these tracers. The chromatograms for the series of five experiment systems, representative of a larger group of experiments, have used the initial reactant conditions given in Table 1. The experiments include: (1) ISO/ozone (O₃), (2) ISO/O₃/*n*-hexane, (3) irradiated ISO/NO_x (gas-phase prod-

ucts), (4) irradiated ISO/NO_x (SOA), and (5) ISO/NO_x in the presence of acidic sulfate aerosol.

Two additional experiments (6, 7) with irradiated ISO/OH in the absence of NO_x were carried out to determine to what extent the HOM tracers appear at low NO_x conditions. For experiment (2) the *n*-hexane added scavenged OH formed during ozonolysis. Gas-phase products detected in experiment (3) provide a comparison with tracer compounds found in the particle phase.

Two groups of products were found in each of the four particle-phase systems, albeit at various concentrations. Figure 1 displays GS-MS chromatograms of the two groups of products detected in the five different experiments. Group 1 consists of seven HOM tracers: 2-methyltartronic acid (MTtA), 2-methylthreonic acid (2MTtA), 2-methylerythronic acid (2MeTA), 3-methylthreonic acid (3MTtA), 3-methylerythronic acid (3MeTA), *erythro*-methyltartaric acid (eMTA), and *threo*-methyltartaric acid (tMTA). These are easily seen in panel 4 of Figure 1 from the isoprene/NO_x irradiation. These compounds have been given in Table 2 in the order of GC retention times. Table 2 gives the chemical formulas, O:C mass ratio, the five most abundant ions associated with each TMS derivative in methane-CI mode, the molecular weights of the underivatized (MW) and TMS-derivatized compounds (MW_{BSTFA}), exact masses from LC-HRMS analysis for the corresponding [M – H][–] pseudomolecular ions, and the proposed chemical structures of the compounds. Group 2 compounds are the previously reported isoprene particle phase tracer compounds, 2MGA, 2MTtT, and 2MeT, and are also detected in the experimental systems reported in this study.^{9,10,13,35,40,45} Figure 1 shows that in the isoprene-O₃ experiment (panel 1) all seven group 1 tracer compounds are at levels equal to or substantially lower than those of traditional isoprene group 2 tracers. Moreover, once the OH scavenger is added to the same system (panel 2), the group 1 tracers all but disappear. The group 1 tracers are substantially present in the particle phase from the isoprene oxidation in the presence of NO_x (panel 4), although they again are generally below the level of detection in the gas phase (panel 3).

As indicated from the comparison of experiments (1) and (2), OH radicals play the dominant role in the formation of the Group 1 tracers. Samples collected from experiments (6) and (7) (Table 1) using an XAD-denuder are characteristic of the gas phase. The gas- and particle-phase products from the NO_x-

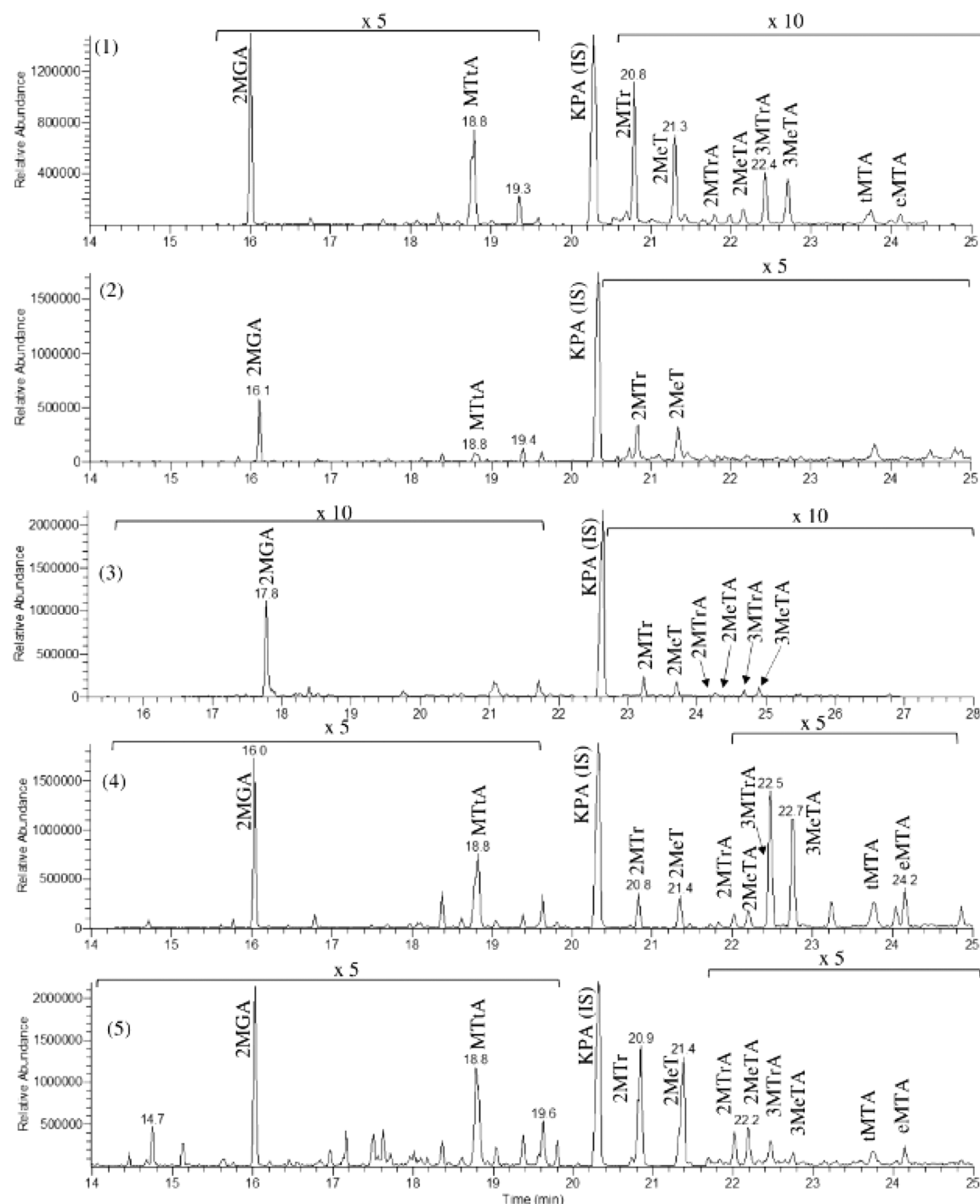


Figure 1. GC-MS extracted ion chromatograms of products associated with the oxidation of isoprene. Ions extracted are m/z 321 (2-methylglyceric acid, 2MGA), m/z 335 (2-methyltartronic acid, MTtA), m/z 409 (2-methylthreitol, 2MTr; 2-methylerythritol, 2MeT), m/z 423 (2-methylthreonic acid, 2MTTrA; 2-methylerythronic acid, 2MeTA; 3-methylthreonic acid, 3MTTrA; 3-methylerythronic acid, 3MeTA), and m/z 437 (erythro-methyltartaric acid, eMTA; threo-methyltartaric acid, tMTA). The m/z 165 (ketopinic acid, KPA) represents the internal standard used. The different experiment types (1)–(5) are noted in the panels. Retention times may differ due to differing chromatographic conditions.

free irradiation are shown in Figure 2. The gas-phase products are identified as 2-methyl-4-hydroxybut-2-enal and 3-methyl-4-hydroxybut-2-enal (collectively MHB) and are labeled in the Master Chemical Mechanism as HC4CCHO and HC4ACHO, respectively.⁴⁸ They elute at respective retention times of 13.05 and 14.39 min and are completely absent from the particle phase, given they are volatile and have an O:C ratio of 0.53. In contrast, among group 1 compounds in Figure 2a, tMTA and

eMTA (collectively MTA) are the compounds detected in the particle phase only, as shown in Figure 2b. Their relatively high O:C ratio of 1.60 contributes to their condensation into the particle phase.

Figure 2a also shows a significant gas-phase presence of the group 2 tracers (2MGA and MTs). The origin of these gas-phase components is of considerable interest due to previous assumptions that they are formed exclusively in the particle

Table 2. Isoprene HOMs Identified in Isoprene Experiments^f

IUPAC/common nomenclature	Formula	O/C Mass ratio (by wt)	<i>m/z</i> BSTFA Derivative (methane-Cl)	MW (MW _{BSTFA}) Exact mass [M – H] ⁺ (error) (g mol ⁻¹)	Proposed Structure ^e
2-hydroxy-2-methyl-1,3-propanedicarboxylic acid/2-methyltartronic acid (MTtA) ^a	C ₄ H ₆ O ₅	1.67	335, 261, 217, 379, 73	134 (350) 133.0139 (+ 0.0009)	
threo-2,3,4-trihydroxy-2-methyl-1-butanecarboxylic acid/2-methylthreonic acid (2MTrA) ^b	C ₅ H ₁₀ O ₅	1.33	423, 117, 73, 393, 349	150 (438) 149.0454 (+ 0.0009)	
erythro-2,3,4-trihydroxy-2-methyl-1-butanecarboxylic acid/2-methylerythronic acid (2MeTA) ^b	C ₅ H ₁₀ O ₅	1.33	423, 117, 73, 393, 349	150 (438) 149.0454 (+ 0.0009)	
threo-2,3,4-trihydroxy-3-methyl-1-butanecarboxylic acid/3-methylthreonic acid (3MTrA) ^c	C ₅ H ₁₀ O ₅	1.33	423, 349, 73, 147, 393	150 (438) 149.0454 (+ 0.0009)	
erythro-2,3,4-trihydroxy-3-methyl-1-butanecarboxylic acid/3-methylerythronic acid (3MeTA) ^c	C ₅ H ₁₀ O ₅	1.33	423, 349, 73, 147, 393	150 (438) 149.0454 (+ 0.0009)	
threo-2,3-dihydroxy-3-methyl-1,4-butanedicarboxylic acid/threo-methyltartaric acid (tMTA) ^d	C ₅ H ₈ O ₆	1.60	437, 319, 73, 481, 453	164 (452) 163.0246 (+ 0.0008)	
erythro-2,3-dihydroxy-3-methyl-1,4-butanedicarboxylic acid/erythro-methyltartaric acid (eMTA) ^d	C ₅ H ₈ O ₆	1.60	437, 319, 73, 481, 453	164 (452) 163.0246 (+ 0.0008)	

^aNot detected by LC-HRMS. ^b2MeTA and 2MTrA coelute by LC-HRMS given as 2MTrA. ^c3MeTA and 3MTrA coelute by LC-HRMS given as 3MTrA. ^deMTA and tMTA coelute by LC-HRMS given as MTA. ^eFor all compounds except MTtA only one diastereoisomeric formula is shown for simplicity. ^fThe *m/z* values are ordered by increasing retention times. Exact masses for the parent compounds are from the Orbitrap LC-HRMS analyses.

phase.^{9,10} Their presence in the gas phase might result from decomposition of particle-bound oligomers⁴⁹ or by conventional particle–gas partitioning. However, the substantial amounts in the gas phase, particularly for the methyltetrols, suggests a potential gas-phase mechanism.^{49,50} These observations serve as the basis for a revised mechanism presented by Jaoui et al.⁴²

3.1. Structural Characterization of 2MeTA, 3MeTA, 2MTrA, 3MTrA, eMTA, tMTA, and MTtA. Representative EI and CI mass spectra for the BSTFA derivatives of group 1 tracers are presented in Figures S1 and S2 (section S4) in the Supporting Information. For the GC-MS interpretation, the CI mass spectra are generally the best starting point for establishing empirical formulas and structures of the ISO-HOMs. Generally, for TMS derivatives of acids, the CI mass spectra show a strong base peak of the $M^+ + 1$ or $M^+ - 15$ ion which allows inference of their molecular weights. In contrast, the peak for $M^+ + 1$ is very weak or missing in the EI spectra, whereas the $M^+ - 117$ peak is found at high abundance in both EI and CI spectra, indicative of the presence of one or more organic acid groups.⁴¹ Additional distinctive ions allowed differentiation between derivatized acid and alcohol groups, and the expected molecular ions were observed.⁴¹

As a descriptive example, two sets of two peaks are found in the Figure 1 (panel 4) chromatogram. The retention times are

22.03 and 22.20 min for the first set and 22.49 and 22.76 min for the second set. The four peaks display similar fragment and adduct ions across the range *m/z* 50–500 Da. The compounds corresponding to these four peaks are 2MTrA, 2MeTA, 3MTrA, and 3MeTA, respectively. For example, the CI spectrum in Figure S2b, which corresponds to the robust peak eluting at 22.49 min (3MTrA in Figures 1–4), shows characteristic product ions at *m/z* 73, 423 [$M^+ - 15$], 349 [$M^+ - 89$], 321 [$M^+ - 117$], 333 [$M^+ - 105$], and 305 [$M^+ - 133$], and adduct ions at *m/z* 439 [$M^+ + 1$], 467 [$M^+ + 29$], and 479 [$M^+ + 41$]. The same set of product ions is also present in the later-eluting compound (3MeTA) at 22.76 min. This ionic pattern is consistent with the presence of four OH groups, the molecular weight (MW) of 438 Da for the derivatized compound and 150 Da molecular weight for the parent compound with the two peaks representing two diastereomers. Mass spectral peaks at *m/z* 321 [$M^+ - 117$] and 333 [$M^+ - 105$] are consistent with a compound having both carboxylic acid (COOH) and alcoholic (OH) functional groups.^{38,41} In contrast, the EI spectrum has far greater fragmentation and only a subset of these peaks is present (e.g., the EI base peak of *m/z* 73 representing the TMS group).

Figure 1 (panel 4) shows two peaks eluting approximately 1.0 and 1.5 min after 3MeTA (RT = 22.72 min) having some of the same identifying fragments and adducts as the 2MTrA,

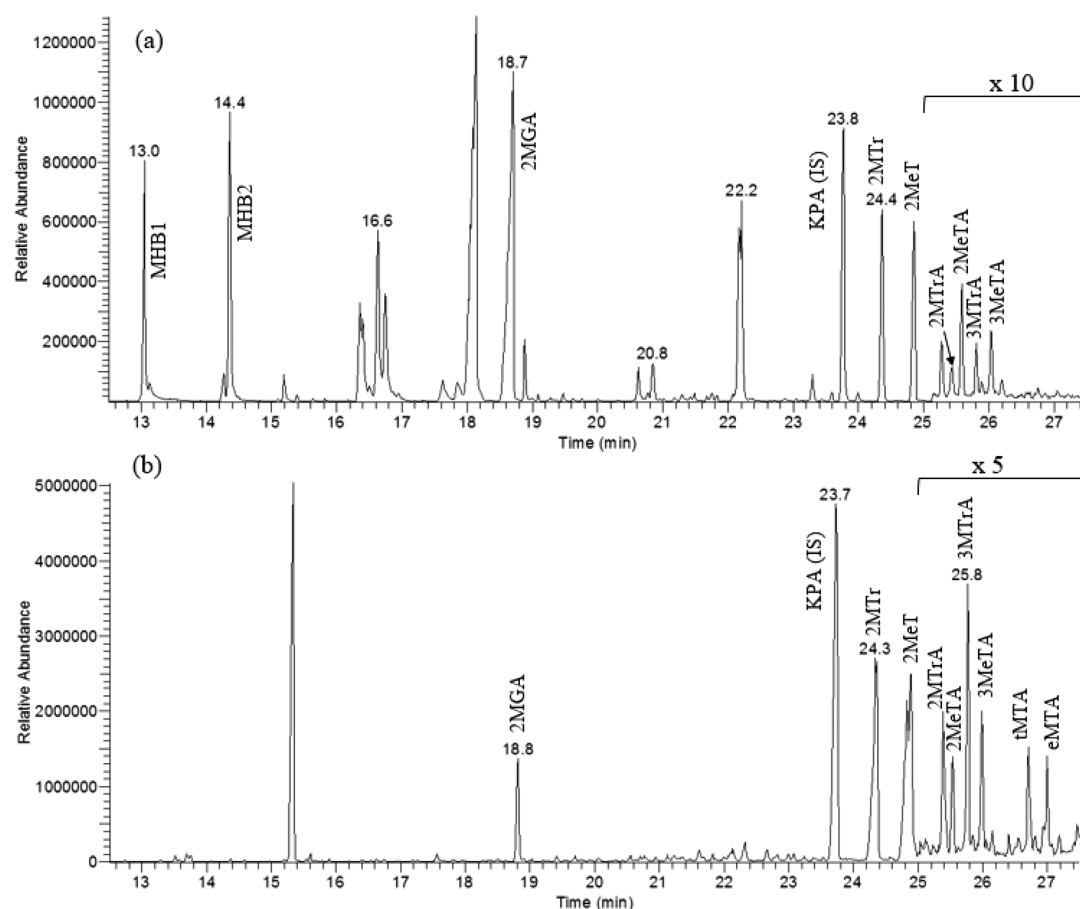


Figure 2. (a) Gas-phase and (b) particle-phase tracer compounds in experiments with the irradiation of an isoprene/ H_2O_2 mixture, which produces OH in the absence of NO_x . The gas-phase extracts from denuder samples were analyzed by GC-MS. Methyltetrols and isomers of methylthreonic acid appear to partition between the gas and particle phases, while the methyltartaric acids are absent from the gas phase presumably because of their low volatility (high O:C ratio).

3MTTrA, 2MTTrA, and 3MeTA compounds. These compounds are detected in all SOA samples from Figure 1 except for the isoprene/ozone/hexane system (Figure 1, panel 2) where they are below the limit of detection. This observation suggests the importance of photochemical systems where OH is present. The EI and CI mass spectra associated with the first peak ($\text{RT} = 23.72$) are shown in Figure S2c,d, respectively. The CI mass spectrum shows TMS-characteristic ions at m/z 73 and 147. Identifying fragments were found at m/z 437 [$\text{M}^+ - 15$], 363 [$\text{M}^+ - 89$], 319 [$\text{M}^+ - 133$], and adducts at 453 [$\text{M}^+ + 1$], 481 [$\text{M}^+ + 29$], and 493 [$\text{M}^+ + 41$]. These fragments and adducts are consistent with the presence of four OH groups and a MW of 452 Da for the derivatized compound and 164 Da for the parent compound. The EI fragmentation of m/z 437 [$\text{M}^+ - 15$], 363 [$\text{M}^+ - 89$], and other ions are consistent with the CI analysis. The two peaks have been identified as threo-methyltartaric acid (tMTA) and erythro-methyltartaric acid (eMTA), respectively.

Figure 2 shows two extracted ion chromatograms from the isoprene/ H_2O_2 experiment associated with the gas (a) and particle phase (b), respectively. Ions extracted are m/z 165 (KPA), m/z 321 (2MGA), m/z 335 (MTtA), m/z 409 (2MTTr, 2MeT), m/z 423 (2MTTrA, 2MeTA, 3MTTrA, 3MeTA), m/z 437 (eMTA, tMTA), and m/z 83 (MHB). The mass spectra for the two early peaks in the gas-phase spectrum ($\text{RT} = 13.05$, 14.39 min) are shown in Figure S3 and correspond to the isomeric hydroxy-methyl-butenals (MHB1, MHB2). Both

mass spectra follow the well-established pattern of fragments and adducts described above. From the analysis, each compound has a derivatized mass of 172 Da and a nominal parent mass of 100 Da. A detailed interpretation of the GC-MS data reveals the presence of single OH and carbonyl groups and an empirical formula of $\text{C}_5\text{H}_8\text{O}_2$. The compounds have also been detected in the NO_x systems, but at far lower intensities. These compounds are believed to be the first-generation oxidation products of isoprene that may possibly oxidize further to produce the ISO-HOM tracers as discussed in a detailed mechanism presented by Jaoui et al.⁴²

For the LC-HR Orbitrap MS/MS analysis, mass spectra of selected laboratory-synthesized compounds 2MTTrA, 3-MTrA, and MTA (section S1 in the Supporting Information) have been used to verify the isoprene product identifications in the laboratory and field extracts. For example, the proposed structures of 3MTTrA, 2MTTrA, and 2MTA were confirmed with LC-Orbitrap MS analysis (Figure 3a,b) by a comparison of the retention time and mass spectral signature of the standard with those from the peak in Figure 1 (panel 4). The registered MS² spectra of standards and analytes are nearly identical (Figure 3c–h). The slightly distorted relative abundances of diagnostic ions observed in the LC-ESI Orbitrap MS/MS spectra of the synthesized standard and the MW 164 unknown from isoprene SOA are explained by the coelution of erythro and threo isomers of MTA during the reversed-phase chromatography.

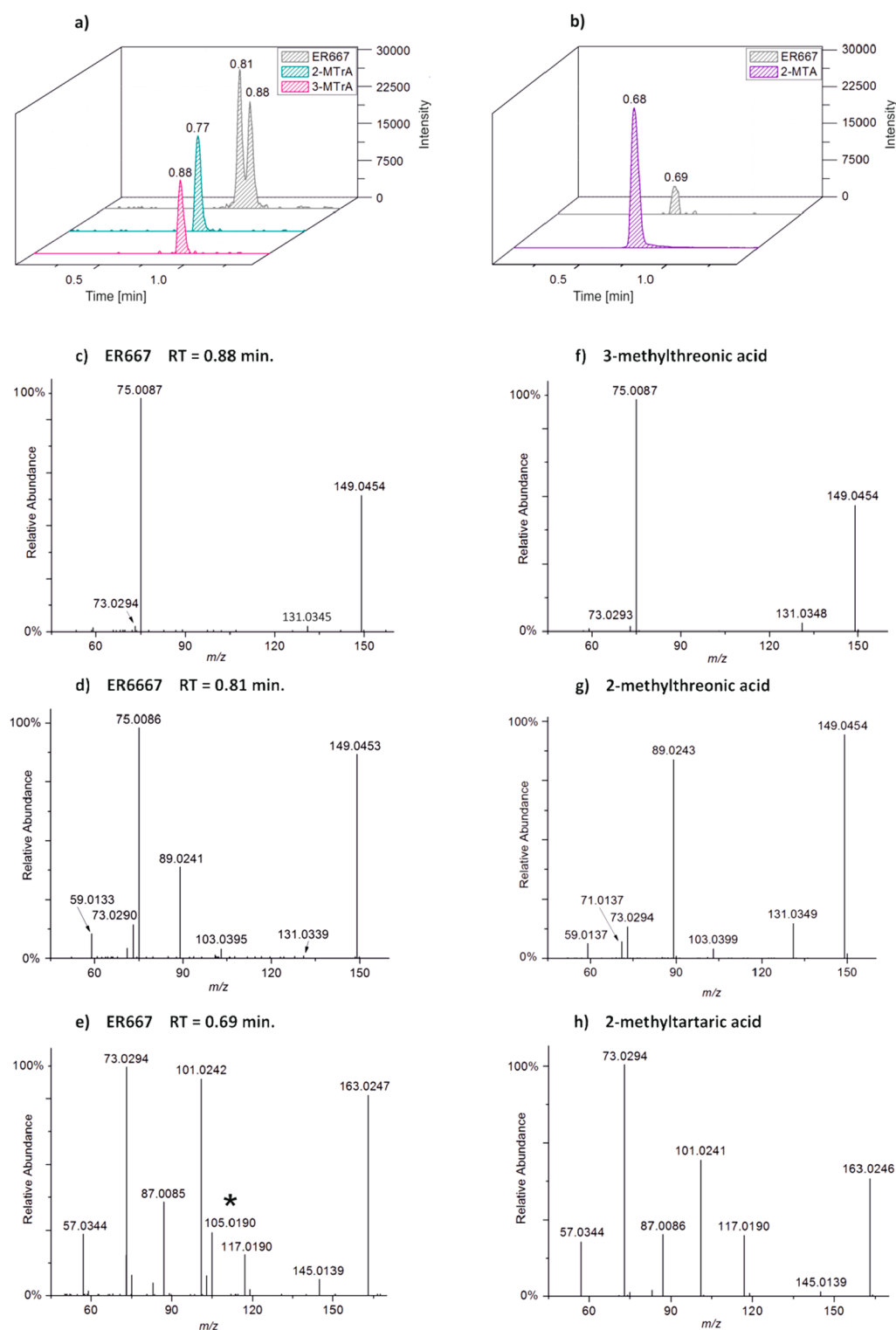


Figure 3. LC-Orbitrap MS extracted ion chromatograms (m/z 149 and 163) acquired for (a, b) ER667 smog chamber SOA and authentic standards. Negative ion electrospray product ion mass spectra (MS^2) of (c) the MW 150 unknown from smog chamber ISO SOA (ER667) eluting at RT 0.88 min, (d) the MW 150 unknown from smog chamber ISO SOA (ER667) eluting at RT 0.81 min, (e) the MW 164 unknown from smog chamber ISO SOA (ER667) eluting at RT 0.69 min, (f) 3-methylthreonic acid, (g) 2-methylthreonic acid, and (h) 2-methyltartaric acid. The asterisk (*) indicates the contamination of the MS system.

The proposed patterns for 3MTrA, 2MTrA, and MTA fragmentation are given in Figure S4.

The LC-HR Orbitrap MS/MS analysis provides spectra having highly accurate mass data that remove possible ambiguities for molecules having the same nominal mass but

different empirical formulas. Figure 3a,b displays LC-Orbitrap MS extracted ion chromatograms (m/z 149 and 163) for authentic standards of 2MTrA, 3MTrA, and MTA together with SOA from the ISO/ NO_x chamber experiment (experiment (8)). Figure 3c–h displays the product ion mass spectra

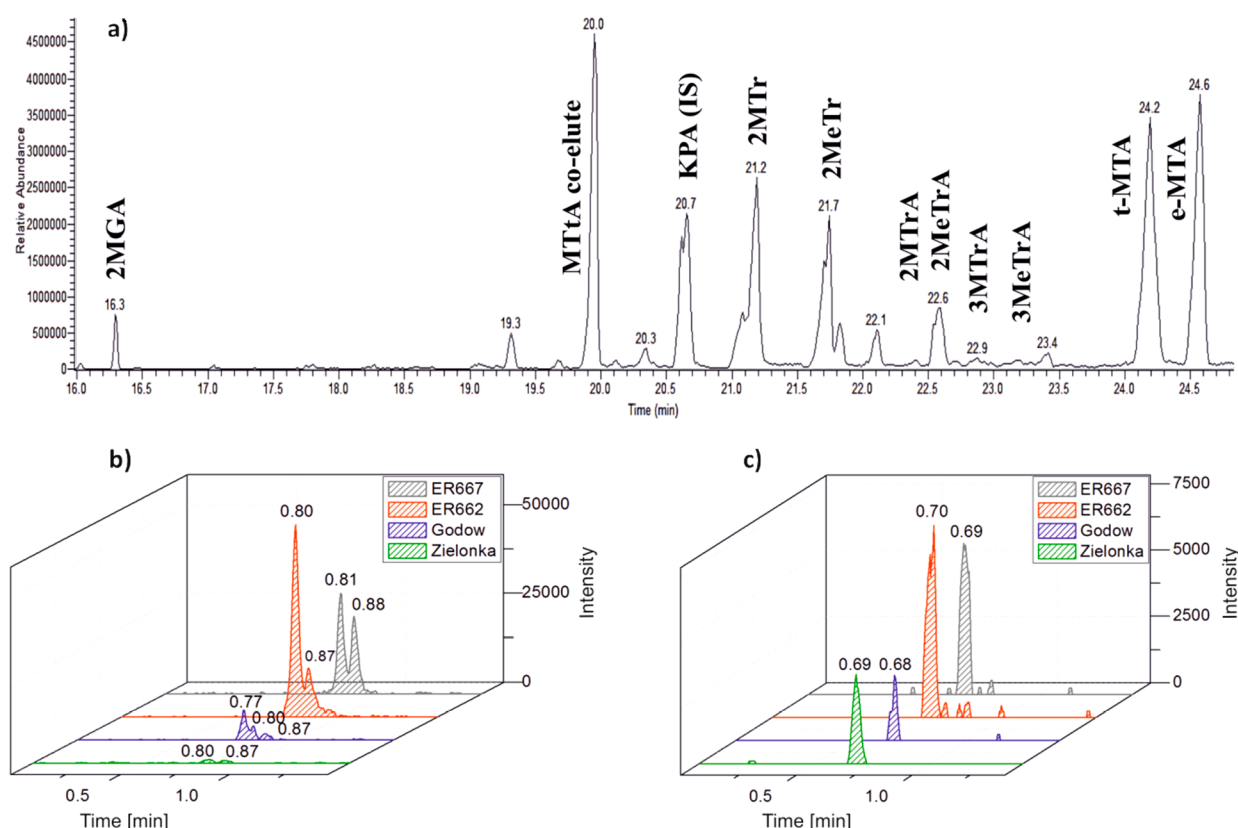


Figure 4. (a) GC-MS extracted ion chromatogram in CI (CH_4) mode from the trimethylsilylated $\text{PM}_{2.5}$ sample collected in summer 2003 at Duke Forest, NC, USA, showing isoprene aging SOA compounds in addition to methyltetrols and 2-methylglyceric acid. Extracted ions are m/z 165, 331, 409, 423, and 437. (b) LC-Orbitrap MS extracted ion chromatograms (m/z 149) and (c) (m/z 163) recorded for ambient fine aerosols collected in Godów and Zielonka (Poland) and for comparison smog chamber ISO SOA generated in the USA. The EPA smog chamber was operated under acidic (ER662) and nonacidic (ER667) conditions.

(MS^2) of a MW 150 unknown from chamber isoprene products eluting at RT 0.88 min (Figure 3c), a MW 150 unknown from the isoprene product eluting at RT 0.81 min (Figure 3d), a MW 164 unknown from the isoprene product eluting at RT 0.69 min (Figure 3e), the standard for 3-methylthreonic acid (Figure 3f), the standard for 2-methylthreonic acid (Figure 3g), and the standard for 2-methyltartaric acid (Figure 3h). The elemental composition of the deprotonated compound shown in Figure 3a,c has an exact mass of 149.0454 Da, thereby giving an empirical formula of $\text{C}_5\text{H}_{10}\text{O}_5$, which is entirely consistent with the GC-MS characterization. This empirical formula has been observed in other studies of isoprene oxidation and is believed to be a major HOM component of isoprene-based PM.³³ Another compound consistently shown by the GC and LC analyses is methyltartronic acid. The peak is the earliest one to elute of the seven compounds. Figure S5 shows the LC-HR Orbitrap MS data of the compound which elutes from an HSS T3 reversed-phase column at 0.73 min (Figure S5a,b) and the TMS derivative from GC-MS analysis (Figure S5d,e). A plausible fragmentation pathway for methyltartronic acid is shown in Figure S5c. Additional mass spectral discussion of MTtA is reported in the section S5 in the Supporting Information.

While the LC-HR Orbitrap MS/MS provides highly reliable empirical formulas for the tracers of the putative ISO-HOMs, the relatively poor resolution power of the liquid chromatography rendered a single peak for the 2MTrA and 2MeTA, similarly to 3MTrA and 3MeTA and the two isomers of MTA

(Figure 3a,b and Figure S5a). In contrast, GC-MS showed a good separation for trimethylsilylated ISO-HOMS isomers (Figures 1 and 2). The presence of two asymmetric carbon atoms (two chiral centers) in isoprene HOM acids (Table 2), except for MTtA, makes each of them exist as a pair of diastereoisomers. Therefore, their formation under atmospheric and/or laboratory conditions may result in a racemic mixture of two statistically possible diastereoisomers. For example, the peak at RT 22.4 min assigned to 3-methylerythronic acid in GC/MS chromatograms (Figure 1, panel 1) corresponds to the equimolar mixture of the stereoisomers (2*R*,3*S*)-2,3,4-trihydroxy-3-methyl-1-butanecarboxylic acid and (2*S*,3*R*)-2,3,4-trihydroxy-3-methyl-1-butanecarboxylic acid. However, the consistency of the GC-MS and LC-Orbitrap MS/MS identifications, together with the use of authentic compound standards, proves that the derivatization process does not compromise the integrity of the parent compounds. At the present time, we find no evidence that MTtA, 2MTrA, 2MeTA, 3MTrA, 3MeTA, tMTA, and eMTA have been previously reported as structurally elucidated particle-phase isoprene oxidation products.

3.2. Detection in Ambient Samples. We established the presence of the compounds from field samples from two campaigns: (1) at Zielonka and Godów, Poland, in summer 2017⁴³ and (2) at Duke Forest, NC, USA, in summer 2003.⁴⁴ Duke Forest samples were extracted, derivatized, and GC-MS analyzed in 2003 at the time of collection, and the resulting chromatograms were reanalyzed for the targeted compounds reported in this study. Figure 4a shows a GC-MS extracted ion

chromatogram of a PM_{2.5} DF sample. A comparison of mass spectra from the laboratory and field samples is shown in Figure S6 as the TMS derivatives of MTA. Minor differences in the abundances between the laboratory and field CI adducts and fragments can occur when (1) the mass spectra are collected under slightly different reagent gas pressures in the ion source and (2) coelution takes the place of other compounds in the field samples (Figure 4a).

Figure 4a shows a subset of the group 1 tracers which appeared at the DF site. The concentrations were estimated in three ambient samples from DF with a single BSTFA derivatization.^{38,41} The method for quantification given in section S6 in the Supporting Information is consistent with our analysis of the group 2 samples. Using the calibration factors from that method, average concentrations for individual compounds were determined. MTtA was not quantified because it coeluted with other constituents. Moreover, 2-MTrA, 2-MeTA, 3-MTrA, and 3-MeTA were found to be minor constituents occurring at low levels in comparison to the MTA. The concentrations for MTA ranged from 1.5 to 6.3 ng m⁻³. By comparison, levels of the group 2 compounds, 2MGA and 2MTr + 2MeT, ranged from 1.2 to 4.4 ng m⁻³ and from 5.3 to 11.9 ng m⁻³, respectively. Our findings suggest that further atmospheric processing of primary isoprene oxygenates might be occurring via the oxidation of terminal hydroxyl groups over a wide range of conditions. Henceforth, using the GC-MS approach, we focus our attention on methyltartaric acid as the most viable atmospheric tracer for aged isoprene aerosol.

These tracer compounds were also detected at Zielonka and Godów using LC-Orbitrap MS (Figure 4b,c). Findings from chamber samples are also presented in Figure 4 for comparison. The production of the group 1 compounds is apparent in the experiments with NO_x (Figure 4b,c). These compounds were confirmed in the field samples by a comparison of the retention times and mass spectral signatures of the standards (Figures 3 and 4). The registered MS² spectra of these HOMs in the field samples are nearly identical with those of the synthesized standards. The ambient PM_{2.5} samples in Figure 4b show modest levels of 2MTrA and 3MTrA, suggesting that they form at low yields rapidly, convert to other compounds, or are removed by another mechanism. From Figure 4c, the peaks eluting at 0.68 and 0.69 min for the PM_{2.5} samples show that MTA is detected in the PM_{2.5} samples in Zielonka and Godów. Note that these HOM compounds were not detected in SOA generated in chamber experiments conducted during the past 15 years from the oxidation of several hydrocarbons, including but not limited to α -pinene, β -pinene; *d*-limonene, Δ^3 -carene, toluene, benzene, *p*-, *m*-, and *o*-xylenes, naphthalene, 1,3-butadiene, a series of C₄, C₅, and C₆ alkenes, dienes, aldehydes, and alcohols, β -caryophyllene, α -humulene, α -cedrene, α -farnesene, β -farnesene, etc.

In summary, we showed that the oxidation of isoprene under a range of conditions produced particle-phase tracers indicative of aged isoprene aerosol. Seven tracer compounds, 2-methyltartronic acid, 2-methylthreonic acid, 2-methylerythronic acid, 3-methylthreonic acid, 3-methylerythronic acid, *erythro*-methyltartaric acid, and *threo*-methyltartaric acid, were identified using molecular structure analysis and confirmed using synthesized standards. Their detection in ambient aerosol samples from selected locations in Europe and the USA provided the evidence that isoprene HOMs are present in ambient aerosol and give molecular evidence for isoprene

aging. The results have potential implications for monitoring and modeling the formation and growth of aerosol in areas affected by isoprene oxidation, for prediction of the properties of aerosol particles, for determination of the uptake of liquid water under humid conditions influencing scattering more incident light, and the formation of cloud droplets.

While the chemical characteristics of SOA products formed from isoprene oxidation have been reported in several studies, this is the first study to find specific isoprene SOA products due to aerosol aging. These hydroxy carboxylic acids are found to be an important class of compounds in isoprene SOA, in that their concentrations in ambient PM_{2.5} samples are near or exceed the levels of the methyltetrols in the same samples. Additional analysis of a wide range of field studies and proposed formation mechanisms are forthcoming.⁴²

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.9b05075>.

Detailed procedures for the preparation of the reference compounds and some of their TMS derivatives, description of chamber experiments, schemes containing the fragmentation pathways, field study information, and discussion of additional derivatization experiments (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*M.J.: e-mail, jaoui.mohammed@epa.gov; tel, 1-919-541-7728.

*R.S.: e-mail, ralf@ichf.edu.pl; tel, 4822 343-3402.

ORCID

Mohammed Jaoui: 0000-0002-2728-9137

Rafal Szmigielski: 0000-0003-3389-9318

Notes

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