1	Supporting information
2	Organic Hydroxy Acids as Highly Oxygenated
3	Molecular (HOM) Tracers for Aged Isoprene
4	Aerosol
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6	Mohammed Jaoui ^{1*} , Rafal Szmigielski ^{2*} , Klara Nestorowicz ² , Agata Kolodziejczyk ² , Kumar Sarang, ² Krzysztof
7	J. Rudzinski ² , Anna Konopka ³ , Ewa Bulska ³ , Michael Lewandowski ¹ , Tadeusz E. Kleindienst ¹
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10	¹ National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park,
11	NC, 27711. ² Environmental Chemistry Group, Institute of Physical Chemistry, Polish Academy of Sciences,
12	01-224 Warsaw, Poland. ³ University of Warsaw, Faculty of Chemistry, Biological, and Chemical Research
13	Centre, 02-089 Warszawa, Zwirki i Wigury 101, Poland.
14	*E-mail: jaoui.mohammed@epa.gov, phone: (919 541-7728); ralf@ichf.edu.pl, phone: (4822 343-3402).
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Section S1. Synthesis of standard compounds: 2-methylthreonic acid, 3-methylthreonic acid, and
methyltartaric acid.

The syntheses of potassium 2,3,4-trihydroxy-2-methylbutanoate (Scheme S1-A, R1) and potassium 2,3,4-trihydroxy-3-methylbutanoate (Scheme S1-A) were carried out in two-stage processes. A first step 21 involved cis-dihydroxylation of 4-methyl-2(5H)-furanone or 3-methyl-2(5H)-furanone, respectively leading 22 to the corresponding lactone cis-diols (Scheme S1-A), whereas a second step was based on the hydrolysis of 23 the resultant lactone cis-diols under alkaline conditions (Scheme S1-B). The synthesis of 2,3-dihydroxy-2-24 methyl-succinic acid was a one-step reaction from 2-methylmaleic acid and entailed cis-dihydroxylation of the 25 C=C bond (Scheme S2).

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32 Scheme S2. A reaction protocol used for the synthesis of 2,3-dihydroxy-2-methyl-succinic acid (2-methyltartaric acid).

35 General procedure for cis-dihydroxylation. Dihydroxylation reaction was performed according to the 36 method of Fattorusso et al. (2011) with small modifications. Potassium osmate dihydrate was added to a 37 solution of corresponding alkene (5.1 mmol), NMO (1.1 g, 10.5 mmol), and citric acid (2.0 g, 10.5 mmol) in tert-BuOH:H₂O mixture (20 mL) then stirred overnight at room temperature. Then the reaction was diluted 38 39 with saturated aqueous Na₂SO₃ (15 mL) and stirred vigorously for 1 hour. The tert-BuOH was evaporated and aqueous layers were extracted with diethyl ether (5 x 15 ml), dried over anhydrous magnesium sulfate, then 40 41 evaporated in vacuo. The residue was purified by flash column chromatography on silica gel 60 (\sim 17 g). The 42 chromatographic conditions and analytical data for the structural characterization of all products synthesized are provided below. 43

The dihydro-3,4-dihydroxy-4-methylfuran-2-one (Y) was isolated after dihydroxylation reaction of 4methyl-2(5H)-furanone as a yellowish oil (0.53 g, 3.6 mmol, 60%) after chromatography on silica gel (
DCM/MeOH, 95:5 → 9:1).

¹H NMR (400 MHz, D₂O) δ 4.41 (s, 1H), 4.24 (s, 2H), 1.38 (s, 3H); ¹³C NMR (101 MHz, D₂O) δ 178.71,
76.15, 75.19, 73.50, 19.74.

The dihydro-3,4-dihydroxy-3-methylfuran-2-one (X) was isolated after dihydroxylation reaction of 3methyl-2(5H)-furanone as a colorless dense oil (0.56 g, 3.8 mmol, 75%) after chromatography on silica gel
(DCM/MeOH, 95:5 → 9:1).

¹H NMR (400 MHz, D₂O) δ 4.54 (dd, J = 10.9, 3.7 Hz, 1H), 4.28 (d, J = 0.6 Hz, 1H), 4.19 (s, 1H), 1.41 (s, 3H); ¹³C NMR (101 MHz, D₂O) δ 180.79, 74.15, 73.17, 73.07, 20.40.

The synthesis of 2,3-dihydroxy-2-methyl-succinic acid was performed according to dihydroxylation protocol described above. The final compound was isolated as a colorless oil (0.42 g, 2.8 mmol, 55%) after chromatography on silica gel (RP-18, MeOH/H₂O, 5:95).

¹H NMR (400 MHz, D₂O) δ 3.29 (s, 1H), 2.99 – 2.75 (dd, 2H), 1.46 (s, 3H). HRMS for Y, m/z: calculated for
 C₅H₇O₆⁻, [M-H]⁻: 163.0243. Found 163.0230.

59 The isolated 1,2-dihydroxylactones **X** and **Y** (Scheme S1-B) (10 mg, 0.075 mmol) were dissolved 60 separately in H₂O (1 mL), whereupon KOH (4.2 mg, 0.075 mmol) was added and the suspension was stirred 61 for 10 minutes at ambient temperature.

62 HRMS for potassium 2,3,4-trihydroxy-2-methylbutanoate (**y**), m/z: calculated for C₅H₉O₅⁻, [M-H]⁻: 63 149.0450. Found 149.0453. HRMS for potassium 2,3,4-trihydroxy-3-methylbutanoate (**x**), m/z: calculated for 64 C₅H₉O₅⁻, [M-H]⁻: 149.0450. Found 149.0455. All analytical data were consistent with previously reported data 65 by Pederson et al. (2009).

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67 Section S2: Field site descriptions

The first site in Poland was a regional background monitoring station located near Zielonka in the 68 Kuyavian-Pomeranian Province (UTM 53°39' N, 17°55' E). The second site was a regional background 69 monitoring station in Godów, located in the Silesian Province in southern Poland (UTM 49°55' N, 18°28' E). 70 71 Detailed characteristics of sampling sites are provided elsewhere (Nestorowicz et al., 2018). In brief, the 72 Zielonka station is located in the forested rural area in Northern Poland, whereas the Godów station is situated in Southern Poland, in the proximity of the large industrial cities of Silesia and near a coal-fired power plant 73 74 in Dětmarovice (Czech Republic). As a result, SOA from the Godów site is strongly influenced by the 75 anthropogenic oxidants, nitrogen oxides, and sulfur dioxide. Both sites have strong isoprene emissions from 76 broad-leaf vegetation of the surrounding forest ecosystems including European oak (Quercus robur, L.), European hornbeam (Carpinus betulus, L.), and Tilia cordata (Tilia cordata, Mill). At both sites, PM_{2.5} samples 77 were collected at 2 m above ground level onto pre-baked quartz-fiber filters using high-volume aerosol 78 79 samplers (DHA-80, Digitel, Switzerland).

For the Duke Forest (Blackwood Division) site in rural Orange County, NC, U.S.A. (UTM 35.978°N, 79.094°W), samples were taken atop a 40-m tower (Geron, 2011). The tower is situated immediately adjacent to a mixed deciduous pine forest having a canopy within 3 m of the top of the tower. Development outside of the site is generally low-density housing and farmland. U.S. Interstate 40 is approximately 2 km to the northeast. During the summer, the prevailing wind direction is from the southwest and the fetch is

predominately from forested areas. Anthropogenic sources of volatile organic compounds in the area are light
and predominately from mobile sources.

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88 Section S3: Description of chamber experiment

89 Initial conditions for the experiments are listed in Table 1 (main paper). Two sets of experiments were 90 conducted. In the first set, four experiments (1-3, 7) were carried out with the chamber operated in a batch-91 mode. In experiments 1, 2, and 7, low volume aerosol (2 to 4 m³) samples were collected on 47-mm glass fiber 92 filters (Pall Gelman Corporation, Ann Arbor, MI) at 9.6 L min⁻¹ and analyzed by GC-MS. Experiments 1 and 93 2 were isoprene ozonolysis conducted without irradiation similar to that of Kleindienst et al., 2007. Experiment 94 3 was conducted with NO_X present to examine the time evolution of gas and aerosol reaction products. Gas and SOA products were collected at 9.6 L min⁻¹ with a 60-cm XAD-4 coated annular denuder and a 47-mm 95 glass fiber filters, respectively. Five consecutive samples were collected during this experiment for 20, 40, 60, 96 97 90, and 130 minutes, respectively. Experiment 7 was isoprene photooxidations using the photolysis of H_2O_2 as the OH source. In the second set, four experiments (4-6, and 8) were conducted with the chamber operated 98 in a flow-mode with a residence time of 4 hours. These conditions produced steady-state mixtures of highly 99 100 oxidized gas-aerosol products. These mixtures could then be extensively sampled under different seed aerosol 101 conditions. For these experiments, the aerosol produced was collected on 47-mm glass fiber filters (Pall 102 Gelman Corporation, Ann Arbor, MI) for 24 hours at 16.7 L min⁻¹ for a total sample volume of 24 m³. GC-MS or LC-MS were used to analyze the organic extracts from these filters. Experiments 3, 4, 5, and 8 were 103 conducted in the presence of NO. Experiment 4 was the baseline isoprene-NO_x irradiation, while Experiments 104 105 5 and 8 explored the effect of humidity or acidity on the isoprene aerosol products. In Experiment 6, OH was generated to oxidize isoprene in the absence of NO_x . The SOA samples were collected using a carbon-strip 106 107 denuder (URG, Inc., Chapel Hill, NC) followed by a 47-mm Teflon-impregnated glass-fiber filter (Pall Gelman Laboratory, Ann Arbor, MI). 108

109 GC-MS conditions. GC-MS analysis was conducted on a ThermoQuest (Austin, TX) GC coupled with 110 an ion-trap mass spectrometer. The injector, heated to 270°C, was operated in the split-less mode. Compounds

111	were separated on a 60-m-long, 0.25-mm-i.d. RTx-5MS column (Restek, Inc., Bellefonte, PA) with a 0.25- μ m
112	film thickness. The GC oven temperature was initiated at 84°C, held for 1 minute, then increased at 8°C min-
113	¹ to 200°C, followed by a 2-minute hold, then an increase at 10°C min ⁻¹ to 300°C and a 15-minute hold. The
114	ion source, ion trap, and interface temperatures were 200°, 200°, and 300°C, respectively. Mass spectra were
115	collected both in the methane-chemical and the electron ionization modes.
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Figure S2. Mass spectra of BSTFA derivatives of 3-methylthreonic acid and t-methyltartaric acid in

143 isoprene SOA in EI and $CI(CH_4)$ modes.



Figure S3. Mass spectra of TMS-ated derivatives of isomeric hydroxy-methyl-butenals detected in isoprene oxidation SOA (methane-CI mode).



Figure S4. Plausible fragmentation routes observed in negative ion electrospray product ion mass spectra of
 a) 3-methylthreonic acid, b) 2-methylthreonic acid, and c) methyltartaric acid.







Figure S6. Mass spectra of BSTFA derivatives of *threo*-methyltartaric and *erythro*-tartaric acid detected in
 samples from chamber isoprene oxidation (top panels) and in ambient PM_{2.5} samples from 2003 Duke Forest
 field study (methane-CI mode, bottom panels).

182 Section S5. Additional discussion of mass spectra for novel isoprene tracers

183 The peak eluting at 18.82 minutes in the isoprene/NO_X irradiation (Figure 1d) appears to be a homolog 184 to 2MGA. The CI mass spectrum of this peak shown in Figure 3e displays identifying fragment ions at m/z335 $[M^+ - 15]$, 261 $[M^+ - 89]$ and adducts at m/z 351 $[M^+ + 1]$, 379 $[M^+ + 29]$, and 392 $[M^+ + 41]$. These 185 ions are consistent with the presence of one OH group and two COOH groups with a parent compound mass 186 187 of 134 Da. Again, the EI fragmentation pattern (Figure 3f) is consistent with that of the CI and show ions at m/z 335 [M⁺ – 15] and 217 [M⁺ – 133]. Based on this evidence, a likely compound associated with this peak 188 is tentatively identified as methyltartronic acid, the structure of which is given as the first entry in Table 2 189 190 (main manuscript). Figure S5 (panels a-b) shows an LC-HRMS trace of methyltartronic acid along with its 191 plausible fragmentation pathways in the ESI ion source (negative mode). The formation of methyltartronic 192 acid is presumed to be formed by the subsequent oxidation of 2-methylglyceric acid, a widely recognized 193 tracer from fresh ISO SOA. At the present time, we find no evidence that MTtA, 2MTrA, 2MeTA, 3MTrA, 3MeTA, tMTA, or eMTA have been previously reported as structurally-elucidated particle-phase isoprene 194 195 oxidation products.

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197 Section S6. Quantification of Tracer Compounds in Field Samples

198 Ouantitative analysis of reaction products of interest in this study shown in Table S1 were performed 199 using a single derivatization with BSTFA. The BSTFA method was evaluated previously (Jaoui et al., 2004, 2006) for quantitative analysis. The most significant sources of error were the surrogate calibration, ion 200 201 extraction uncertainties, and the degree of coelution, especially for the field samples. In this study, a similar 202 quantification method is used. For each compound, the TIC or extracted ion chromatogram of the five most 203 intensive ions were used for quantification, depending on the degree of coelution (see reference Jaoui et al., 204 2006 for more information). Using our best estimate of the calibration factors, concentrations for each of the target compounds for PM_{2.5} samples were determined and provided in Table S1. These values are typical of 205 206 the range of values often seen for individual polar organic compounds detected in ambient samples. Authentic

- standards or surrogates for those that are not available commercially were used for quantification/semi-
- 208 quantification. The field samples were GC-MS analyzed prior to synthesis of authentic standards; therefore no
- 209 authentic standards were used in this study for quantitative analysis.
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- Table S1. Concentration in ng m⁻³ of some compounds measured in three field samples collected in Duke
 Forest, NC during 2003. Their concentration was measured using authentic standards or surrogates (Table S1,
- 213 last column). TC: Total carbon on filter estimated from Sunset instrument (EC-OC analyzed) (Geron, 2011).

	DF2	DF23	DF24	Quantified as
Sampling date	July 10, 2003	July 10, 2003	July 10, 2003	
Duration (hours)	24	49 h 40 min	104 h 25 min	
TC (ugC)	778	1609	3383	
2-Methylglyceric acid	4.4	1.182	2.335	pentanedioic acid
2-Methyltetrols	11.9	5.312	7.576	d-threitol
Pinic acid	1.7	0.48	0.641	pinic acid
3-Carboxy heptanedioic acid	15.1	4.434	5.305	d-Arabitol
3-Hydroxy glutaric acid	5.6	1.27	1.908	tartaric acid
Levoglucosan	7.5	2.279	1.339	levoglucosan
b-caryophyllinic acid	0.6	0.221	0.393	pinic acid
2-Methylthreonic acid	0.69	0.12	0.36	citramalic acid
3-Methylthreonic acid	0.22	0.09	0.04	citramalic acid
Methyltartaric acid	6.27	1.52	2.69	tartaric acid

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