Characterization of Organosulfates in Secondary Organic Aerosol Derived from the Photooxidation of Long-Chain Alkanes

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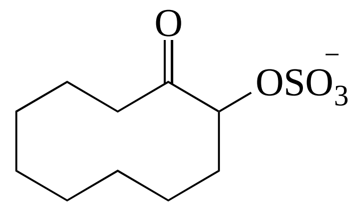
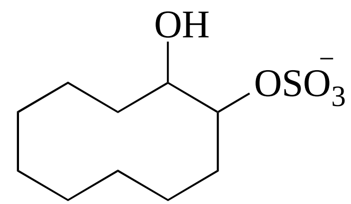
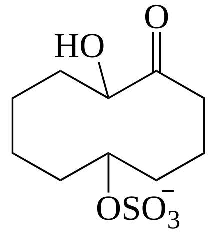
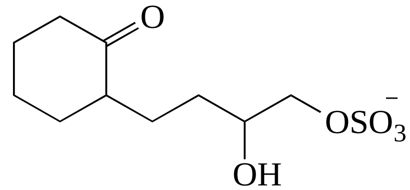
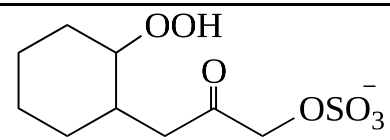
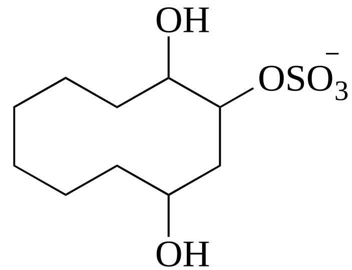
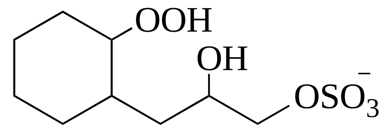
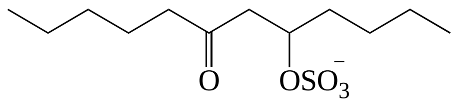
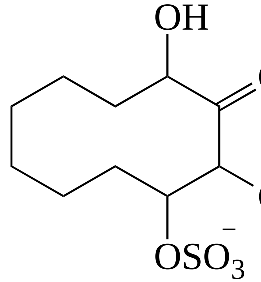
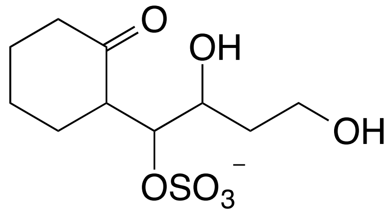
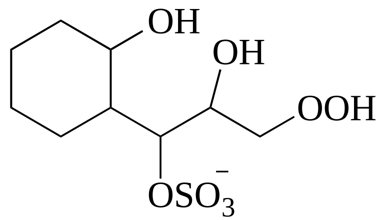
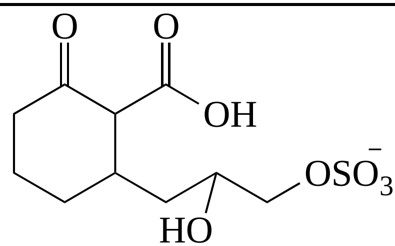
This supporting information contains 25 pages: 4 Tables and 16 Figures.

Table S1. Proposed structures, retention times, formulas and accurate masses of organosulfates (OSs) identified in dodecane, decalin and cyclodecane SOA.

[M - H]$^-$ ion (m/z)	VOC	Retention time (min)	Measured mass	Error (ppm)	Q-TOFMS suggested formula	DBE	Proposed structure
195	Decalin	7.93	195.0697	3.03	$C_7H_{15}O_4S^-$	0	Not Identified
209	Dodecane	6.75	209.0472	5.62	$C_7H_{13}O_5S^-$	1	Not Identified
237	Dodecane	9.12	237.0786	4.67	$C_9H_{17}O_5S^-$	1	Not Identified
249	Cyclodecane	8.51 9.31	249.0807 249.0797	2.84 1.5	$C_{10}H_{17}O_5S^-$	2	
251	Cyclodecane	8.51 9.31	251.0950 251.0953	1.28 0.10	$C_{10}H_{19}O_5S^-$	1	
255	Dodecane	8.87	255.0914	4.56	$C_9H_{19}O_6S^-$	1	Not Identified

265	Cyclodecane	6.40	265.0747	1.41	$C_{10}H_{17}O_6S^-$	2	
265	Decalin	4.40 5.80 6.75 8.10	265.0749 265.0757 265.0742 265.0754	1.18 4.19 1.45 3.06	$C_{10}H_{17}O_6S^-$	2	
267	Decalin	6.38 7.20	267.0553 267.0550	0.02 2.55	$C_9H_{15}O_7S^-$	2	
267	Cyclodecane	8.98 9.61	267.0914 267.0903	2.16 1.70	$C_{10}H_{19}O_6S^-$	1	
269	Decalin	8.04	269.0696	0.73	$C_9H_{17}O_7S^-$	1	
279	Cyclodecane	5.77 6.76	279.0554 279.0551	2.05 5.40	$C_{10}H_{15}O_7S^-$	3	Not Identified

279	Dodecane	11.73 12.04 12.44	279.1256 279.1254 279.1265	3.66 4.37 0.43	$C_{12}H_{23}O_5S^-$	1	
281	Cyclodecane	6.98 7.27	281.0698 281.0705	0.64 2.00	$C_{10}H_{17}O_7S^-$	2	
	Decalin	8.01	281.0702	1.20			
285	Decalin	6.22 6.51	285.0651 285.0648	0.95 0.58	$C_9H_{17}O_8S^-$	1	
295	Decalin	6.84 7.10 7.62	295.0495 295.0505 295.0506	1.19 4.44 5.16	$C_{10}H_{15}O_8S^-$	3	

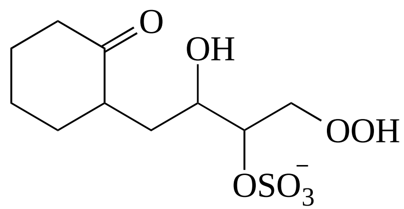
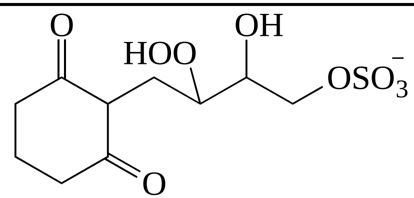
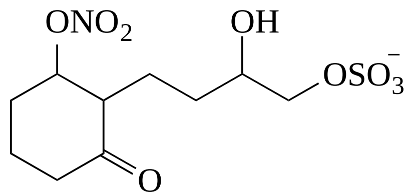
297	Decalin	6.84 7.62 8.30	297.0657 297.0645 297.0652	4.31 0.27 2.63	$C_{10}H_{17}O_8S^-$	2	
299	Decalin	7.65 7.88	299.0805 299.0801	2.05 1.26	$C_{10}H_{19}O_8S^-$	1	Not Identified
307	Dodecane	7.93	307.0833	4.49	$C_{12}H_{19}O_7S^-$	3	Not Identified
311	Decalin	6.57 7.00	311.0444 311.0450	0.23 1.98	$C_{10}H_{15}O_9S^-$	3	
326	Decalin	7.26 8.14 9.38 9.95	326.0551 326.0550 326.0554 326.0557	1.59 1.28 2.51 3.43	$C_{10}H_{16}NO_9S^-$	3	

Table S2. Concentrations (ng m^{-3}) of OSs quantified (using methanol) in dodecane chamber experiments in presence of ammonium sulfate aerosol. Ratios of OS quantified using acetonitrile/toluene (ACN-Tol) divided by OS quantified using methanol as solvent mixture are also reported.

$[M - H]^-$	No-Ac Dry	Ac-Dry	No-Ac Wet	Ac-Wet	Ac-Wet	Ac-Dry	ACN-Tol/Methanol
$C_7H_{13}O_5S^-$ (209.0472)[a,b]	0.58	0.57	0.93	0.92	0.75	0.78	0.99 ± 0.11
$C_9H_{17}O_5S^-$ (237.0786)[a,b]	2.87	2.80	1.97	2.48	3.16	3.54	0.82 ± 0.20
$C_9H_{19}O_5S^-$ (255.0914)[a,b]	2.65	3.10	3.10	3.33	3.66	4.19	0.95 ± 0.20
$C_{12}H_{23}O_5S^-$ (279.1254)[c,d]	1.98	7.76	1.45	2.65	1.75	8.20	1.81 ± 0.37
$C_{12}H_{19}O_7S^-$ (307.0040)[a,b]	0.82	1.18	0.47	0.71	1.41	1.76	1.67 ± 0.43
Sum	8.92	15.41	7.92	10.11	10.74	18.45	1.28 ± 0.12

[a] *Quantified using 3-pinanol-2-hydrogen sulfate ($C_9H_{13}O_6S^-$) as a surrogate standard,* [b] *OSs belonging to Group−2,* [c] *quantified using octyl sulfate as a surrogate standard,* [d] *OSs belonging to Group−1. Different isomers for one ion have been summed; Ac. and No Ac. correspond to acidified and no-acidified sulfate seed aerosol, respectively.*

Table S3. Concentrations (ng m^{-3}) of OSs quantified (using methanol) in decalin chamber experiments in presence of ammonium sulfate aerosol. Ratios of OS quantified using acetonitrile/toluene (ACN-Tol) divided by OS quantified using methanol as solvent mixture are also reported.

$[M - H]^-$	No-Ac Dry	Ac-Dry	No-Ac Wet	Ac-Wet	Ac-Wet	Ac-Dry	ACN-Tol/Methanol
$C_7H_{15}O_4S^-$ (195.0697)[a,b]	26.9	47.4	19.6	29.7	33.1	33.0	0.84 ± 0.23
$C_{10}H_{17}O_6S^-$ (265.0749)[a,c]	12.1	54.3	23.2	49.7	25.5	37.8	1.66 ± 0.45
$C_9H_{15}O_7S^-$ (267.0553)[a,c]	17.3	78.6	23.1	41.3	36.1	70.5	1.81 ± 0.42
$C_9H_{17}O_7S^-$ (269.0696)[a,b]	58.4	72.5	36.5	49.7	61.4	63.0	1.07 ± 0.20
$C_{10}H_{17}O_7S^-$ (281.0702)[a,c]	16.7	61.4	21.0	43.4	22.5	48.1	2.04 ± 0.26
$C_9H_{17}O_8S^-$ (285.0651)[a,c]	48.4	349.6	96.1	279.1	129.4	114.5	1.88 ± 0.55
$C_{10}H_{15}O_8S^-$ (295.0495)[a,c]	41.0	90.3	27.7	46.0	40.7	82.0	2.11 ± 0.75
$C_{10}H_{17}O_8S^-$ (297.0657)[a,b]	16.3	51.5	20.4	37.5	19.1	28.7	2.07 ± 0.38
$C_{10}H_{19}O_8S^-$ (299.0805)[a,c]	6.7	41.7	5.1	8.8	5.2	20.3	1.72 ± 0.37
$C_{10}H_{15}O_9S^-$ (311.0444)[a,c]	20.3	40.2	22.9	36.3	17.5	40.7	2.13 ± 0.26
$C_{10}H_{16}NO_9S^-$ (326.0551)[a,c]	7.9	54.0	38.8	104.4	27.1	71.6	3.03 ± 0.62
Sum	272.0	941.9	334.4	726.0	417.7	610.1	1.78 ± 0.16

[a] *Quantified using 3-pinanol-2-hydrogen sulfate ($C_9H_{13}O_6S^-$) as a surrogate standard,* [b] *OSs belonging to Group−2,* [c] *OSs belonging to Group−1. Different isomers for one ion have been summed; Ac. and No Ac. correspond to acidified and no-acidified sulfate seed aerosol, respectively.*

Table S4. Concentrations (ng m^{-3}) of OSs quantified (using methanol) in cyclodecane chamber experiments in presence of ammonium sulfate aerosol. Ratios of OS quantified using acetonitrile/toluene (ACN-Tol) divided by OS quantified using methanol as solvent mixture are also reported.

$[M - H]^-$	No-Ac Dry	Ac-Dry	No-Ac Wet	Ac-Wet	Ac-Wet	Ac-Dry	ACN-Tol/Methanol
$C_{10}H_{17}O_5S^-$ (249.0807)[a,b]	2.5	48.1	3.9	4.6	3.2	26.5	2.30 ± 0.33
$C_{10}H_{19}O_5S^-$ (251.0950)[a,b]	3.2	39.2	3.8	4.6	4.1	24.4	1.92 ± 0.10
$C_{10}H_{17}O_6S^-$ (265.0747)[a,b]	10.4	40.8	7.4	9.4	5.5	44.0	1.52 ± 0.30
$C_{10}H_{19}O_6S^-$ (267.0914)[a,b]	4.6	39.4	5.0	5.7	9.4	22.9	1.36 ± 0.10
$C_{10}H_{15}O_7S^-$ (279.0554)[a]	*N.d.*	6.4	*N.d.*	*N.d.*	*N.d.*	2.5	
$C_{10}H_{17}O_7S^-$ (281.0698)[a,b]	5.8	28.3	3.9	4.4	4.5	19.3	1.64 ± 0.28
Sum	26.5	202.3	23.9	28.8	26.7	139.6	1.74 ± 0.15

[a] *Quantified using 3-pinanol-2-hydrogen sulfate ($C_9H_{13}O_6S^-$) as a surrogate standard,* [b] *OSs belonging to Group−1. Different isomers for one ion have been summed; N.d.: not detected; Ac. and No Ac. correspond to acidified and no-acidified sulfate seed aerosol, respectively.*

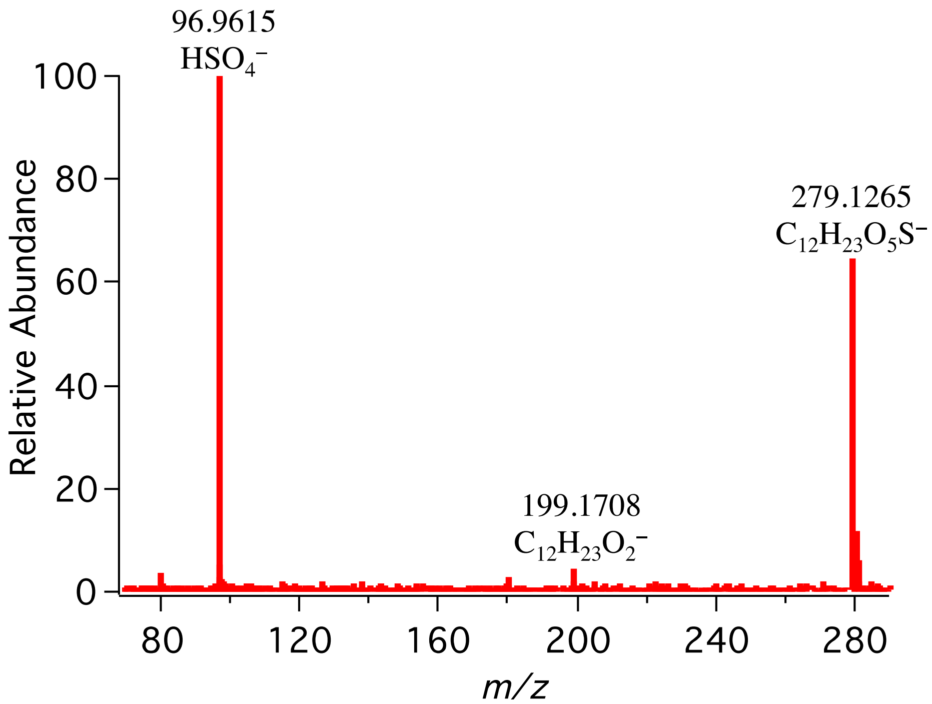
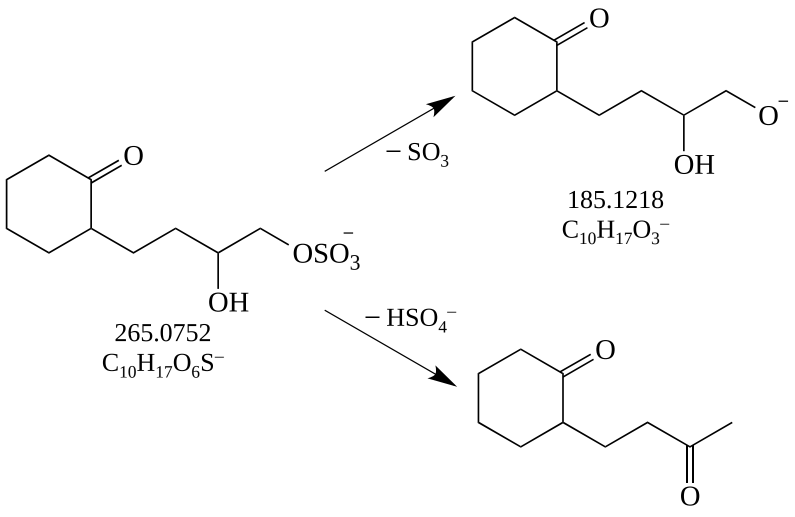
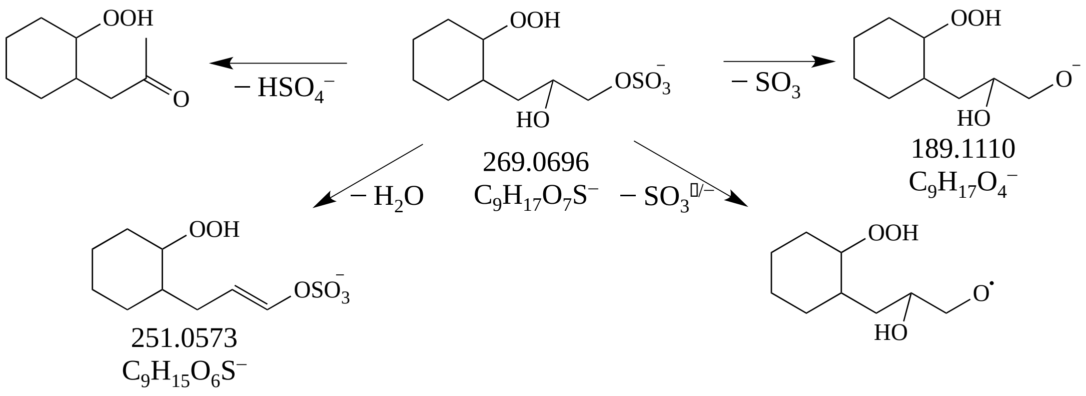


Figure S1. MS^2 spectrum obtained for dodecane-derived OS-279 (*m/z* 279.1274). Fragmentation scheme is proposed in Figure 1.

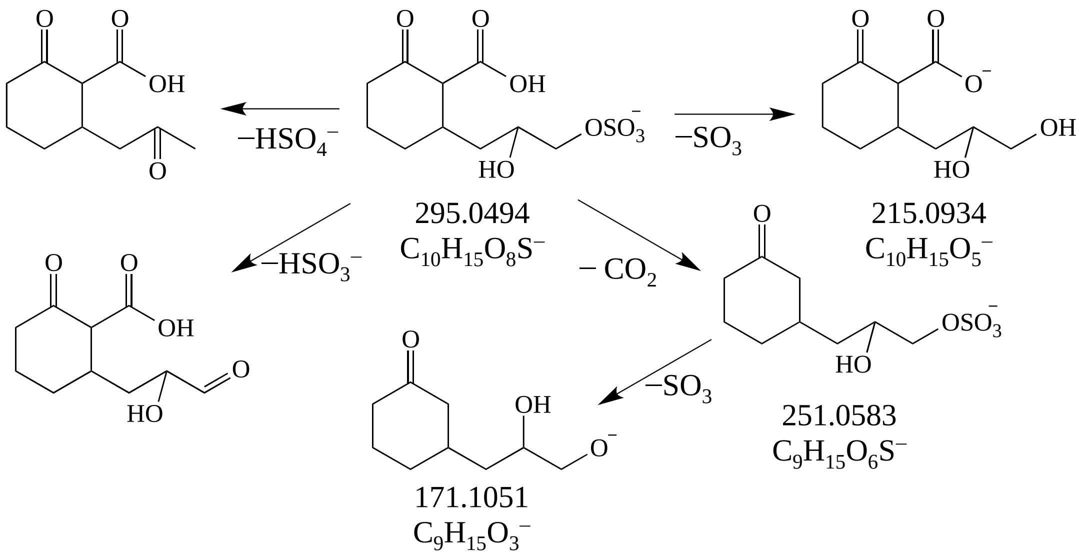
a


O
O
OSO3−
OH
265.0752
C10H17O6S−
− SO3
O−
OH
185.1218
C10H17O3−
− HSO4−
O
O

b


OOH
O
− HSO4−
OOH
OSO3−
HO
269.0696
C9H17O7S−
− SO3
OOH
O−
HO
189.1110
C9H17O4−
− H2O
OOH
OSO3−
251.0573
C9H15O6S−
OOH
O•
HO

c



d

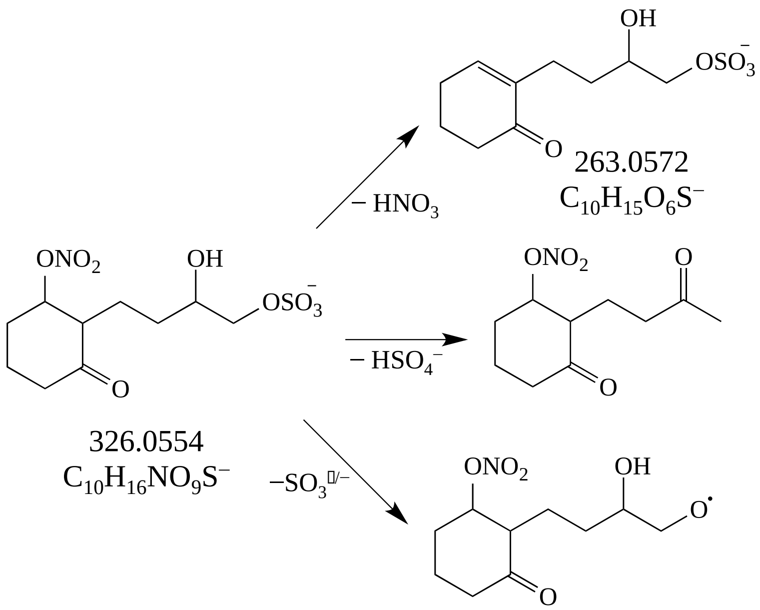


Figure S2. Fragmentation schemes for selected decalin-derived OSs: *a*) *m/z* 265.0752 ($C_{10}H_{17}O_6S^-$), (*b*) *m/z* 269.0696 ($C_9H_{17}O_7S^-$), (*c*) *m/z* 295.0494 ($C_{10}H_{15}O_8S^-$) and (*d*) *m/z* 326.0554 ($C_{10}H_{16}NO_9S^-$). MS^2 spectra are reported in Figure 2.

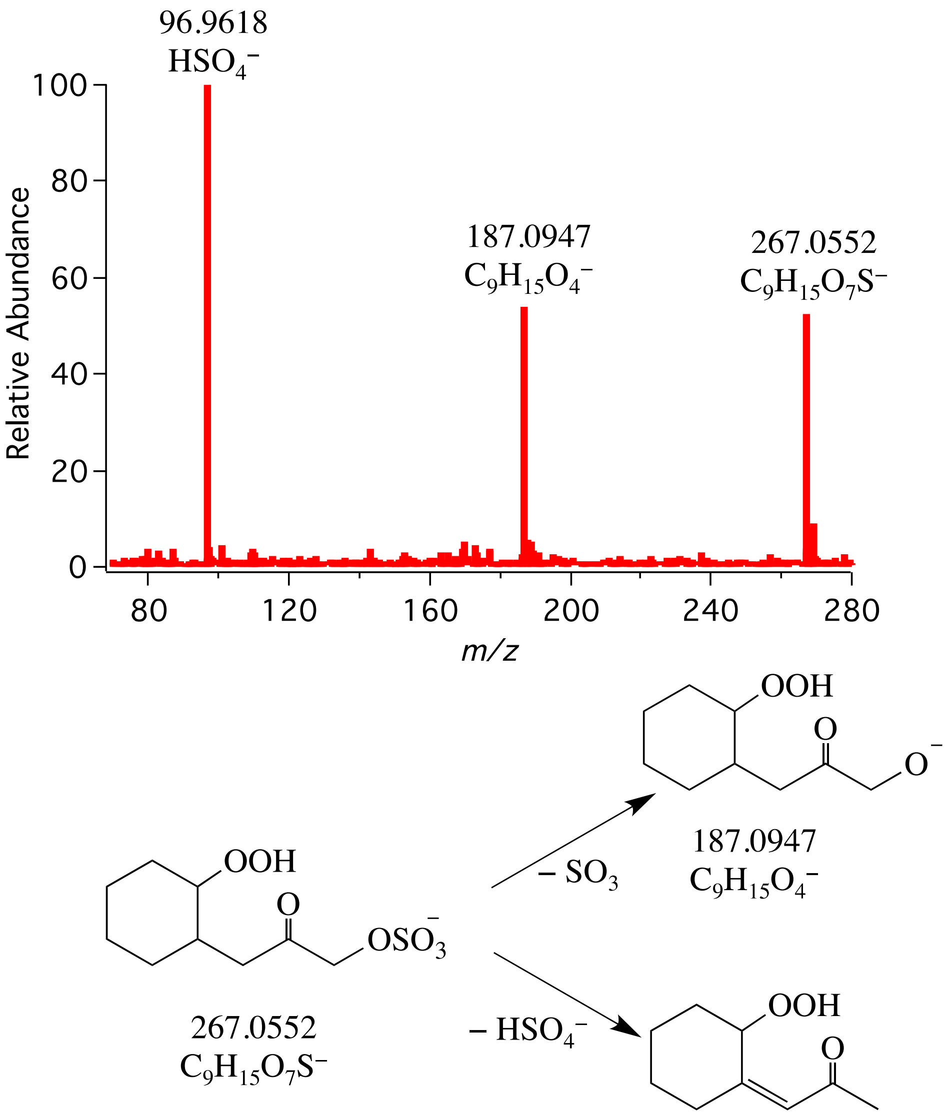


Figure S3. MS^2 spectrum and fragmentation scheme of ion at *m/z* 267.0552 identified in SOA formed from decalin oxidation.

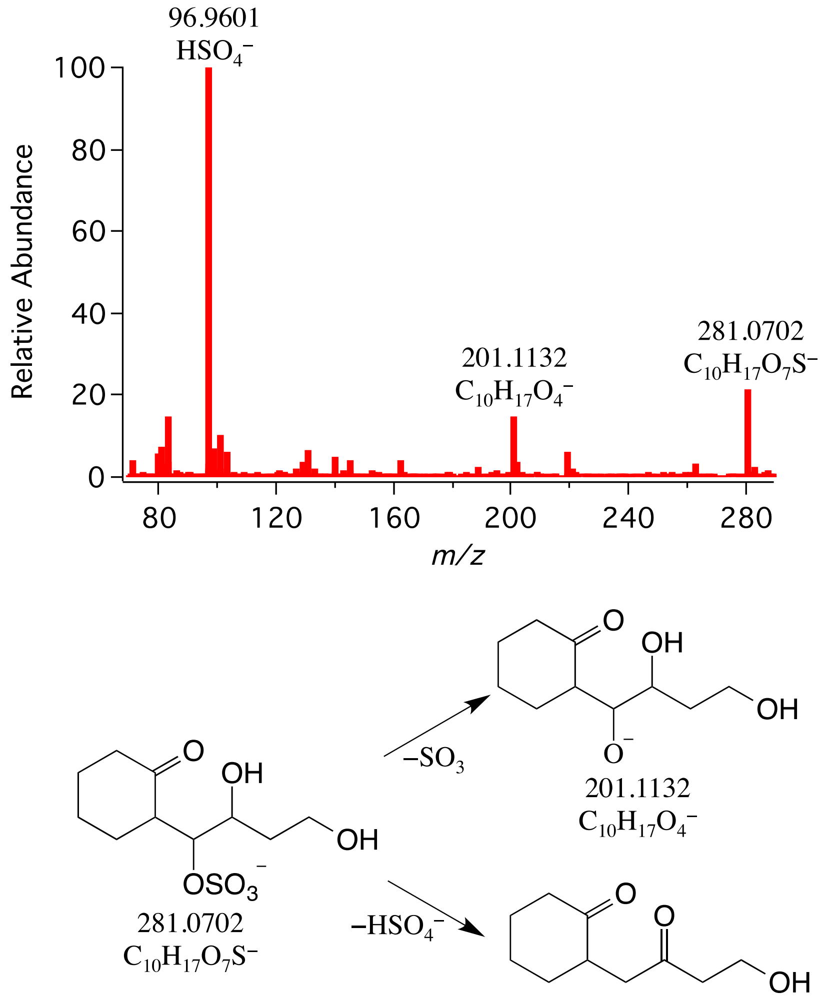


Figure S4. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 281.0702 identified in SOA formed from decalin oxidation.

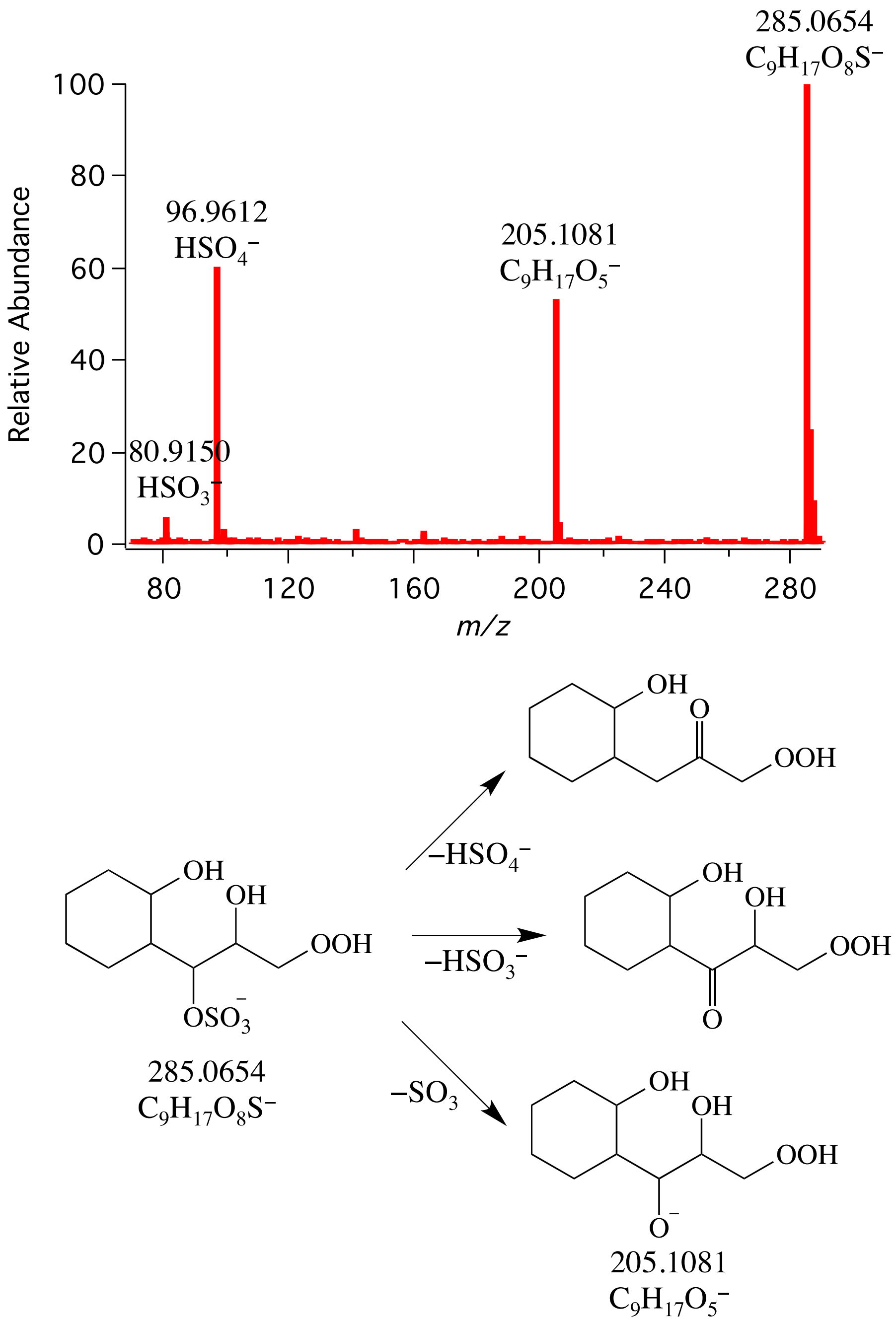


Figure S5. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 285.0654 identified in SOA formed from decalin oxidation.

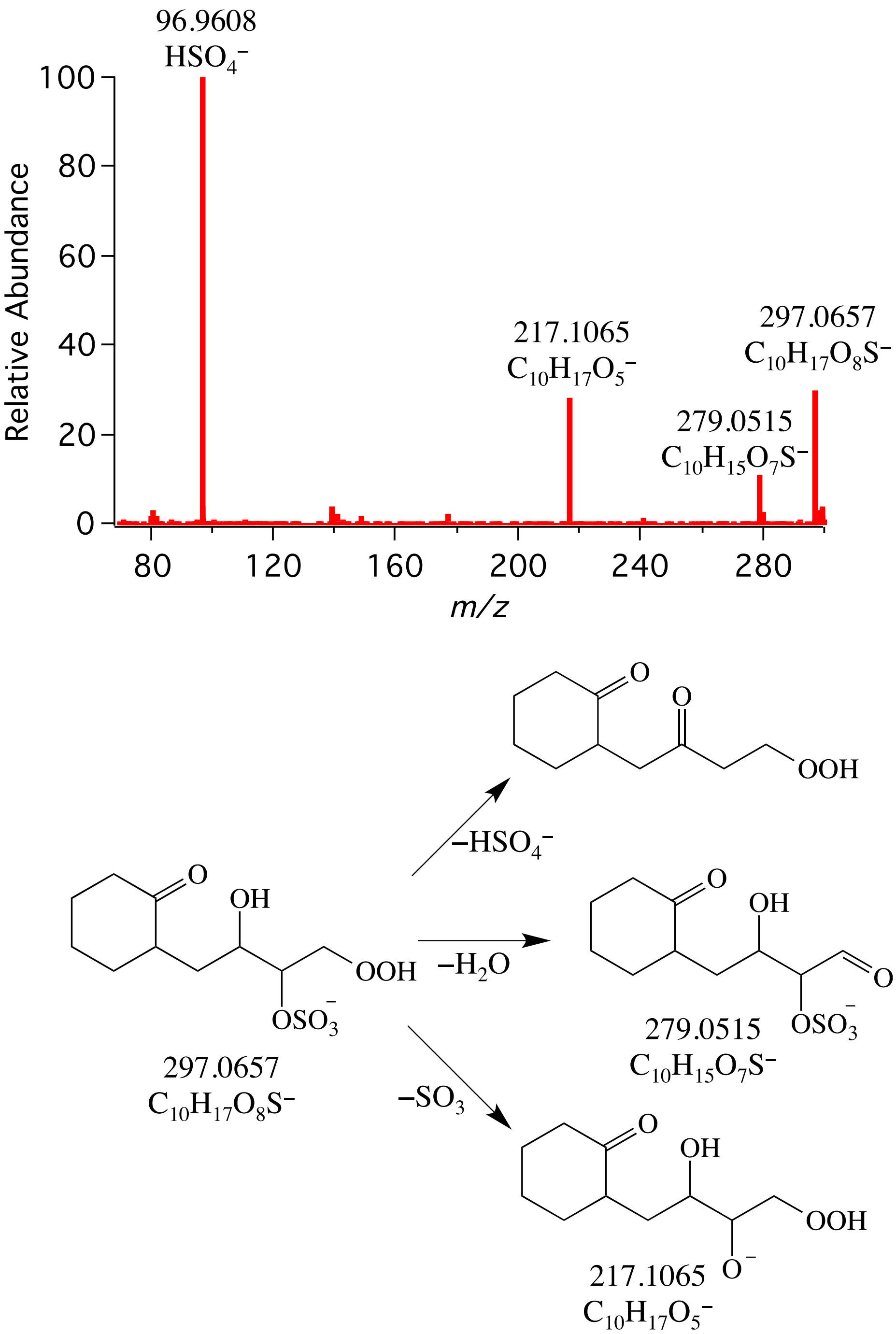


Figure S6. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 297.0669 identified in SOA formed from decalin oxidation.

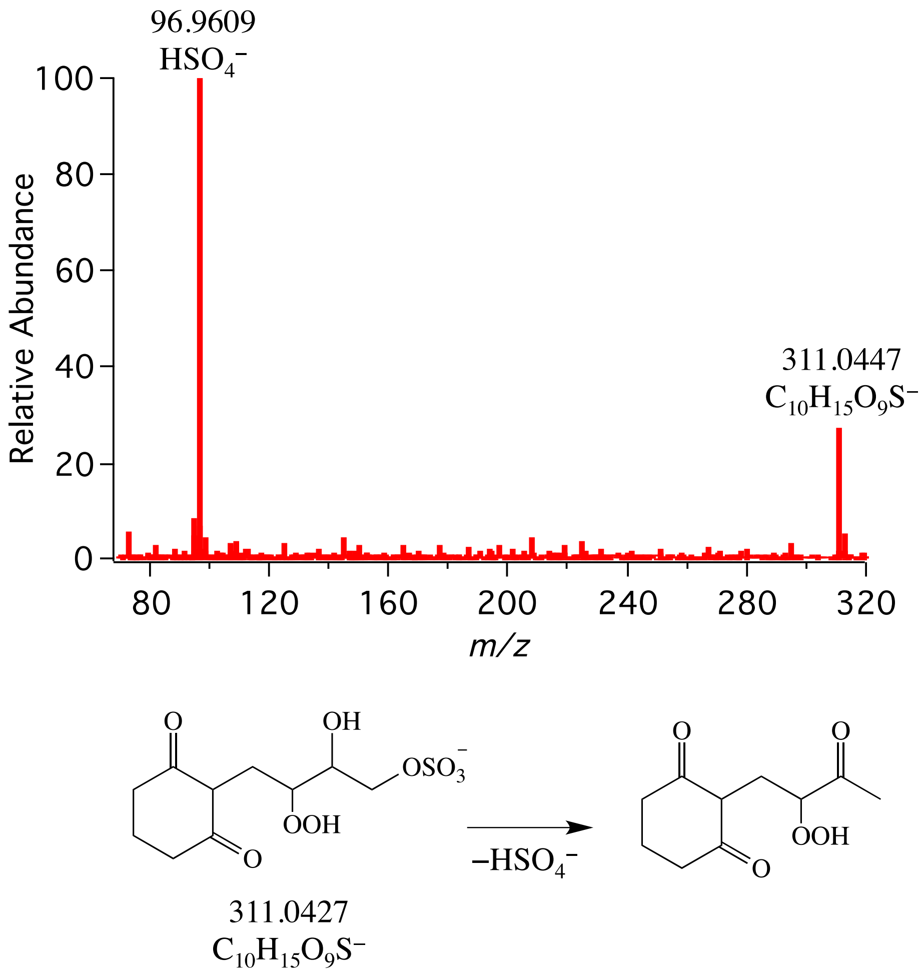


Figure S7. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 311.0427 identified in SOA formed from decalin oxidation.

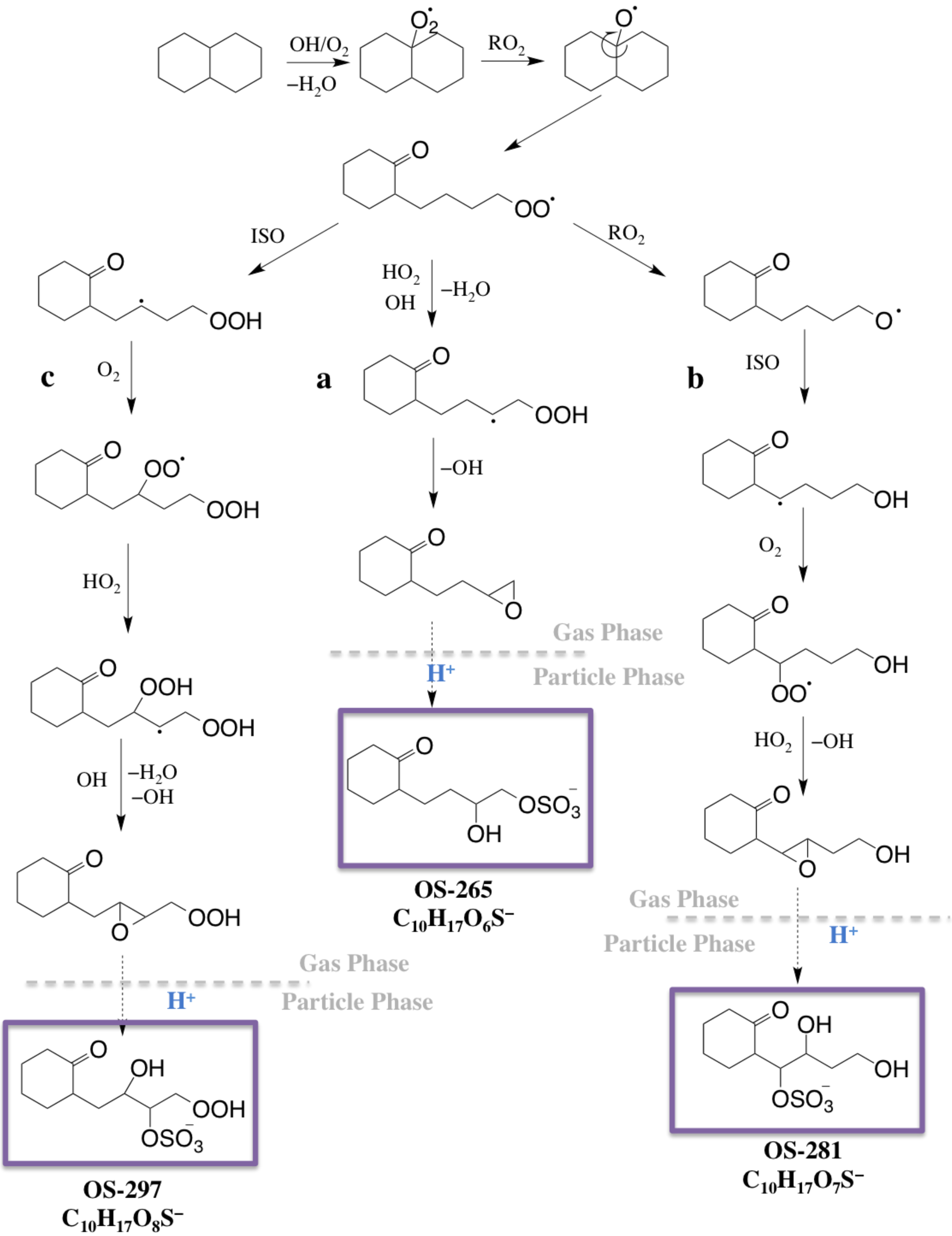


Figure S8. Proposed formation pathways of OS-265, OS-281 and OS-295 from the oxidation of decalin in the presence of ammonium sulfate aerosol. ISO = isomerization reaction either through H shift (1,5- or 1,7-) or through hyderoperoxide isomerization with an R radical.

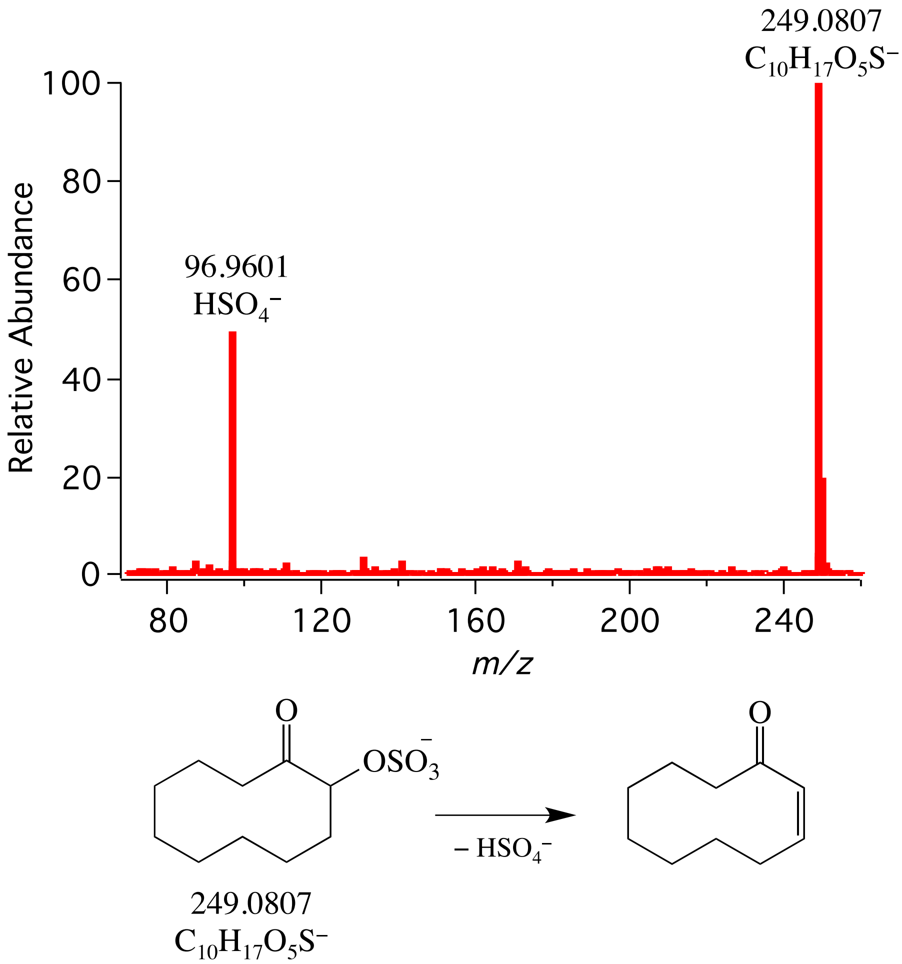


Figure S9. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 249.0807 identified in SOA formed from cyclodecane oxidation.

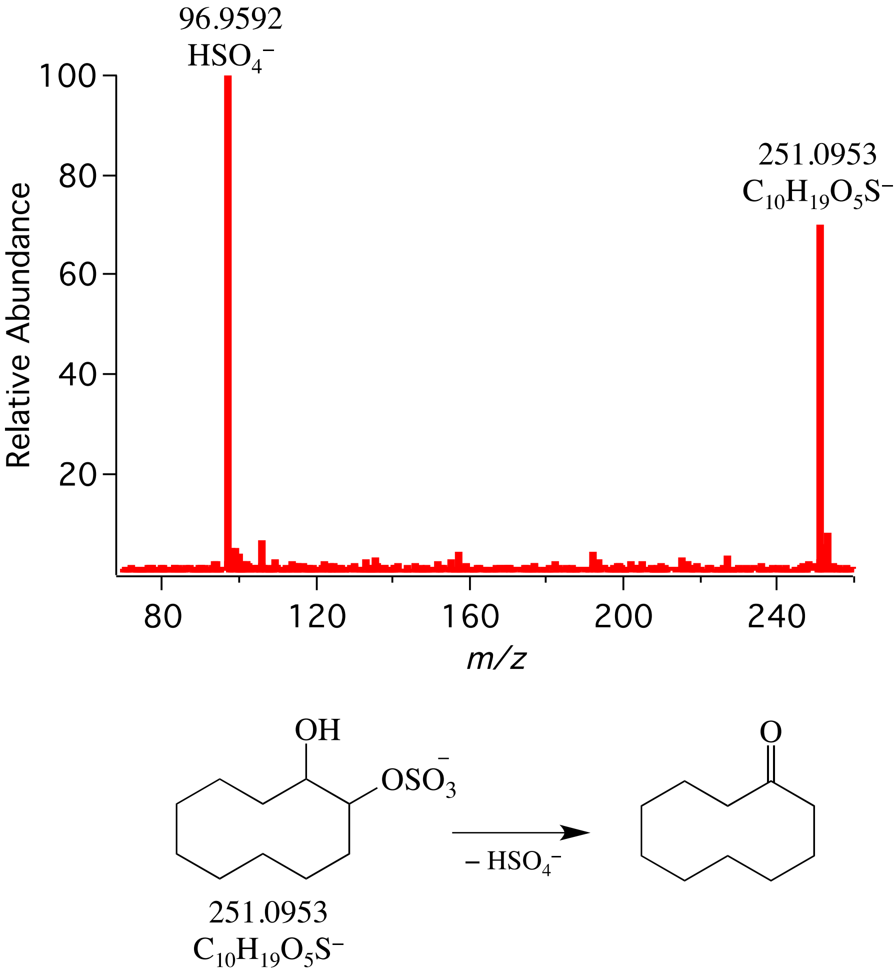


Figure S10. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 251.0953 identified in SOA formed from cyclodecane oxidation.

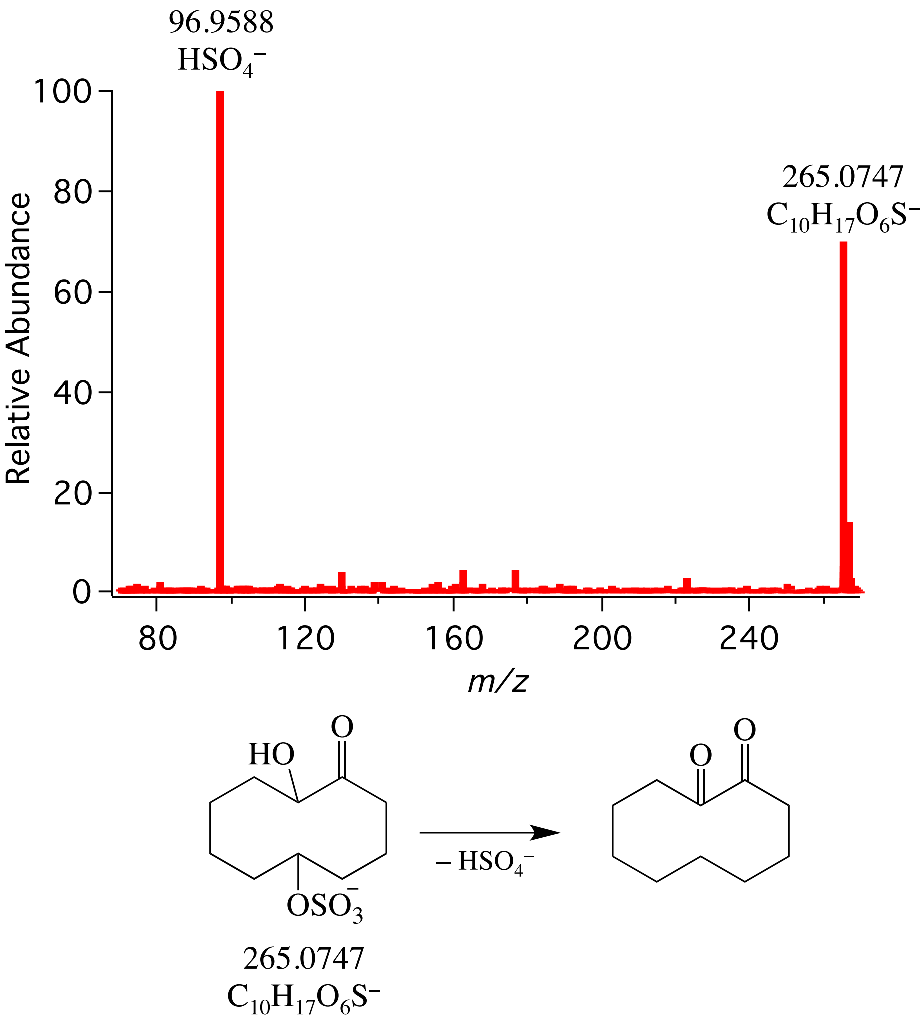


Figure S11. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 265.0747 identified in SOA formed from cyclodecane oxidation.

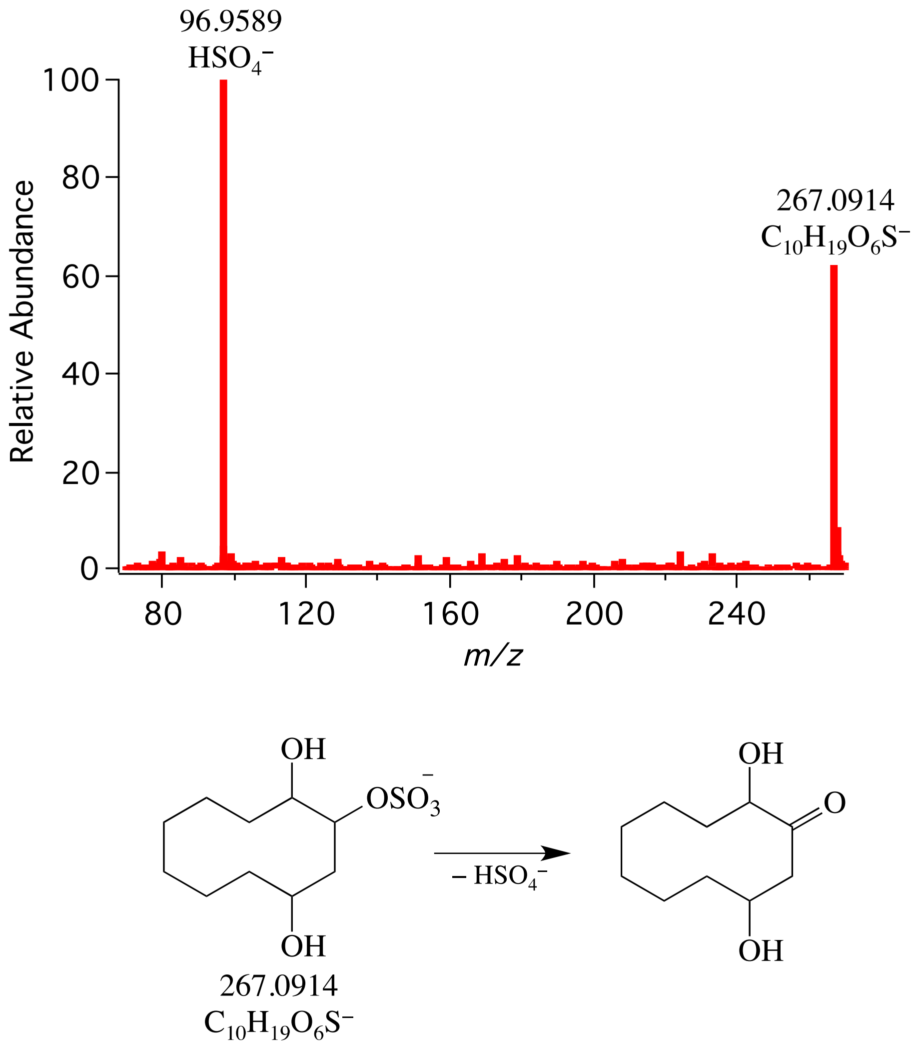
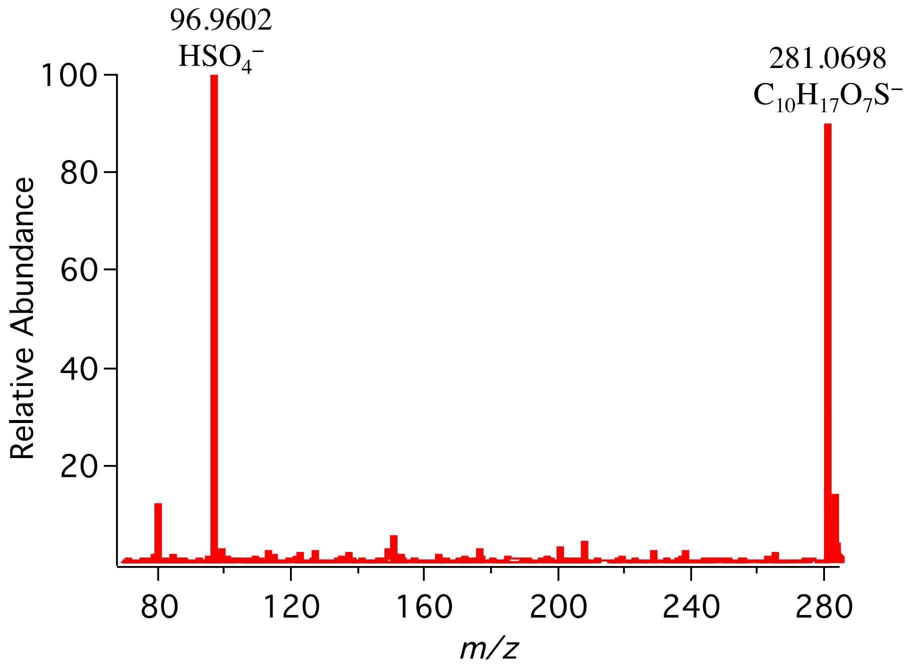


Figure S12. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 267.0914 identified in SOA formed from cyclodecane oxidation.



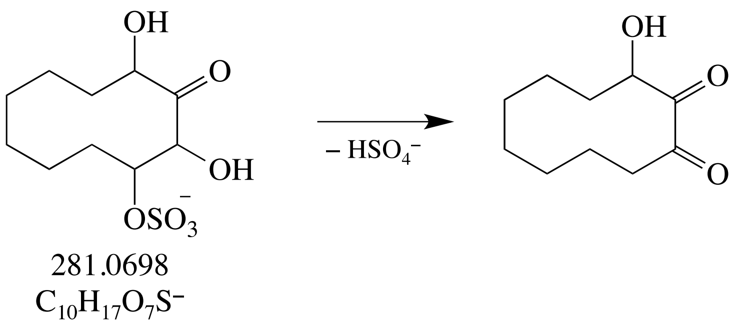


Figure S13. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 281.0698 identified in SOA formed from cyclodecane oxidation.

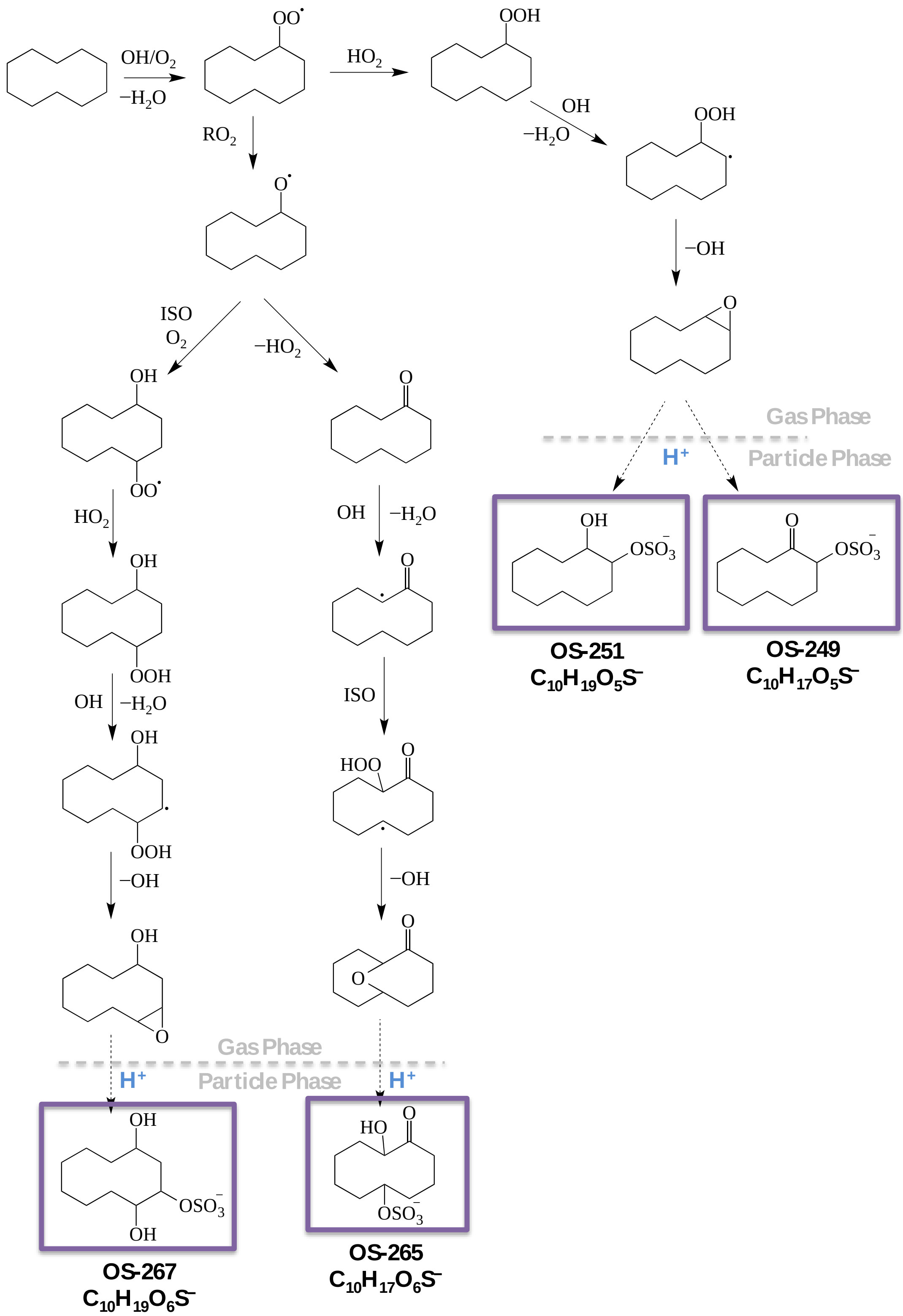
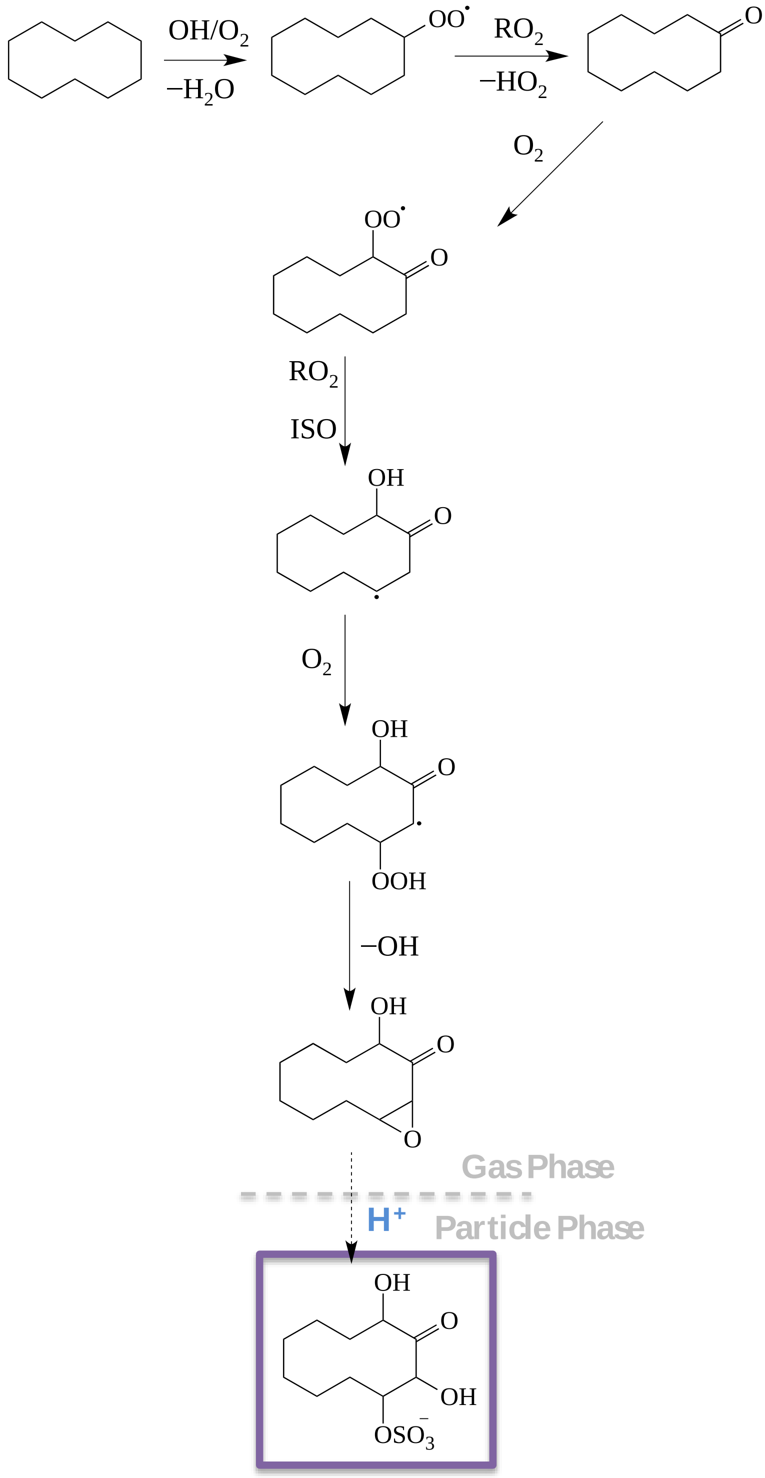


Figure S14. Proposed formation pathways of OS-249, OS-251, OS-265 and OS-267 from the oxidation of cyclodecane in presence of sulfate aerosol. ISO = isomerization reaction either through H shift (1,5- or 1,7-) or through hyderoperoxide isomerization with an R radical.



OS-281
$C_{10}H_{17}O_7S^-$

Figure S15. Proposed formation pathways of OS-281 from the oxidation of cyclodecane in presence of sulfate aerosol. ISO = isomerization reaction either through H shift (1,5- or 1,7-) or through hyderoperoxide isomerization with an R radical.

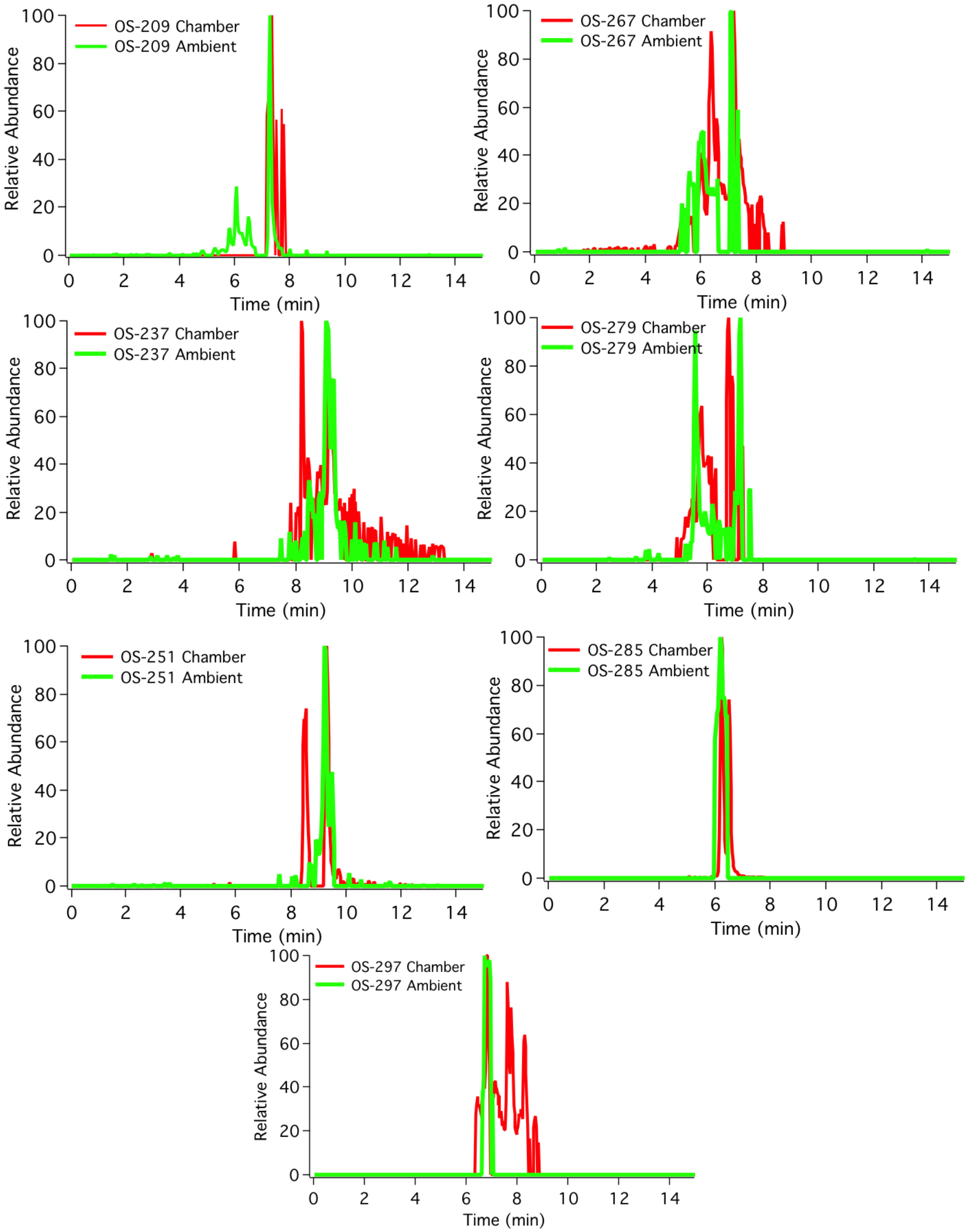


Figure S16. Extracted ion chromatograms (EICs) for alkane-derived OSs identified in aerosol collected from both smog chamber experiments (in red) and field studies (in green).