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Supplement of

Chemical characterization of organosulfates in secondary organic aerosol derived from the photooxidation of alkanes

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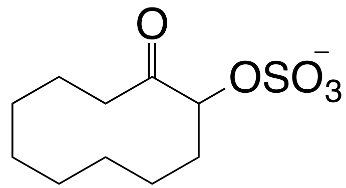
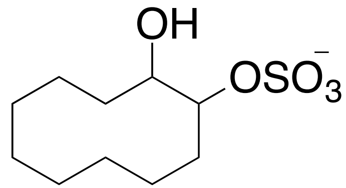
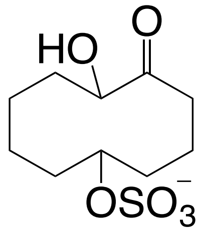
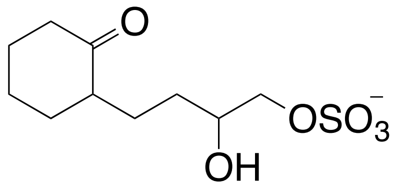
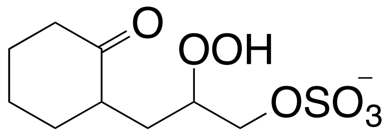
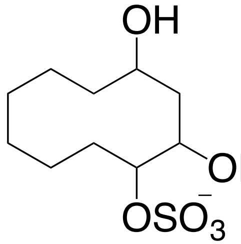
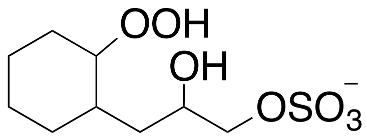
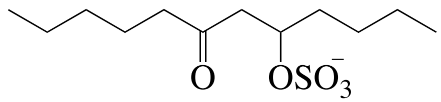
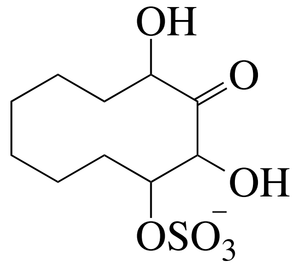
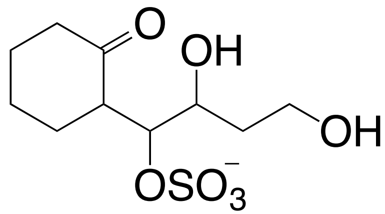
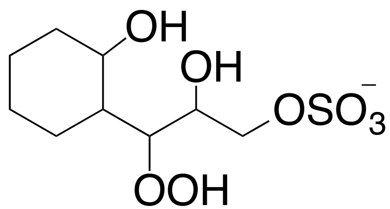
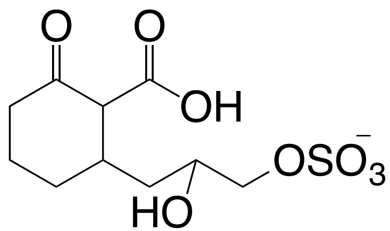
Table S1. Proposed structures, retention times, formulas and accurate masses of organosulfates (OSs) identified in dodecane, decalin and cyclodecane SOA.

[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	249.0807	2.84	$C_{10}H_{17}O_5S^-$	2	
		9.31	249.0797	1.5			
251	Cyclodecane	8.51	251.0950	1.28	$C_{10}H_{19}O_5S^-$	1	
		9.31	251.0953	0.10			
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

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

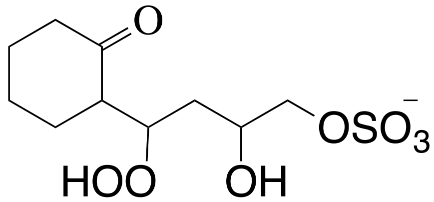
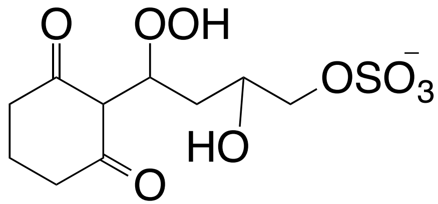
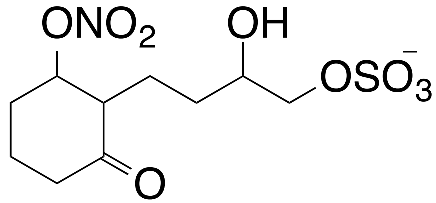
297	Decalin	6.84 7.62 8.30	297.0657 297.0645 297.0652	4.31 0.27 2.63	$C_{10}H_{17}O_8S^-$	2	
299	Decalin	7.65 7.88	299.0805 299.0801	2.05 1.26	$C_{10}H_{19}O_8S^-$	1	Not Identified
307	Dodecane	7.93	307.0833	4.49	$C_{12}H_{19}O_7S^-$	3	Not Identified
311	Decalin	6.57 7.00	311.0444 311.0450	0.23 1.98	$C_{10}H_{15}O_9S^-$	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.

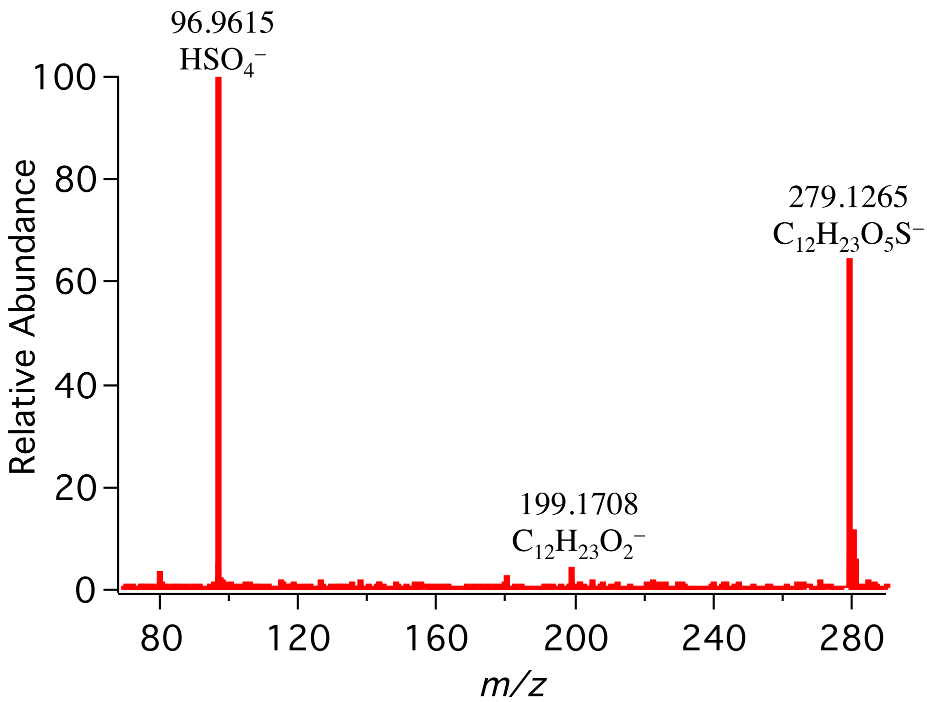
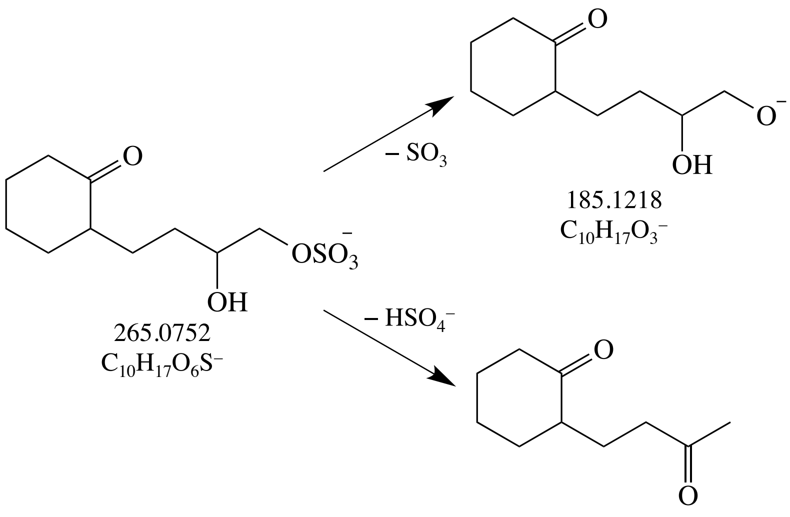
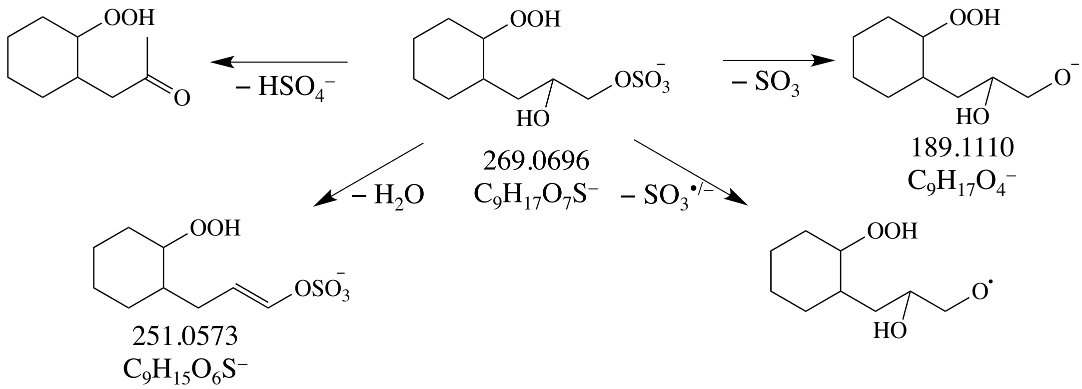


Figure S1. MS^2 spectrum obtained for dodecane-derived OS-279 (*m/z* 279.1274). Fragmentation scheme is proposed in Figure 1.

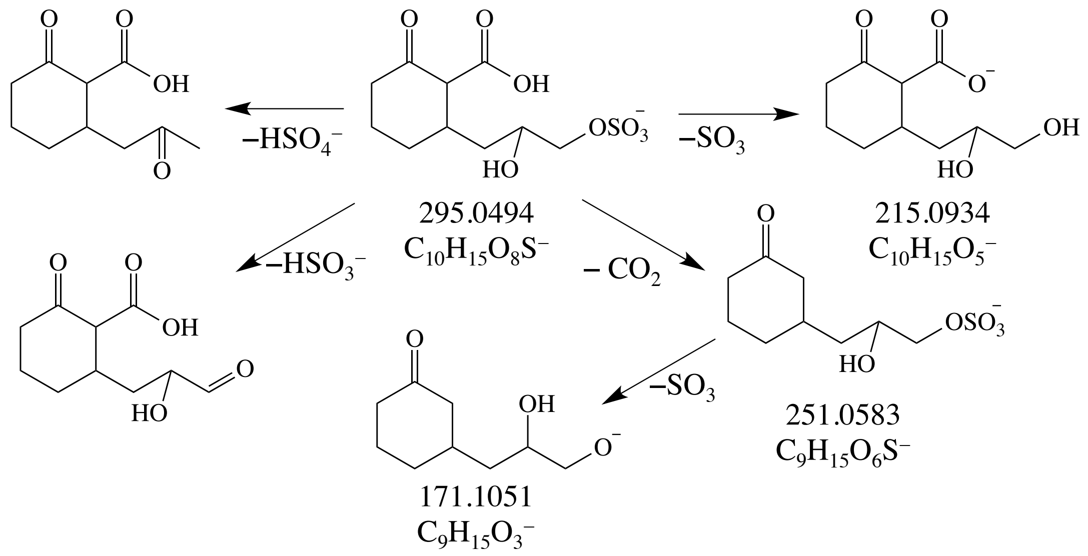
a


O
OSO3−
OH
265.0752
C10H17O6S−
− SO3
O
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−
− SO3•/−
OOH
O•
HO

c



d

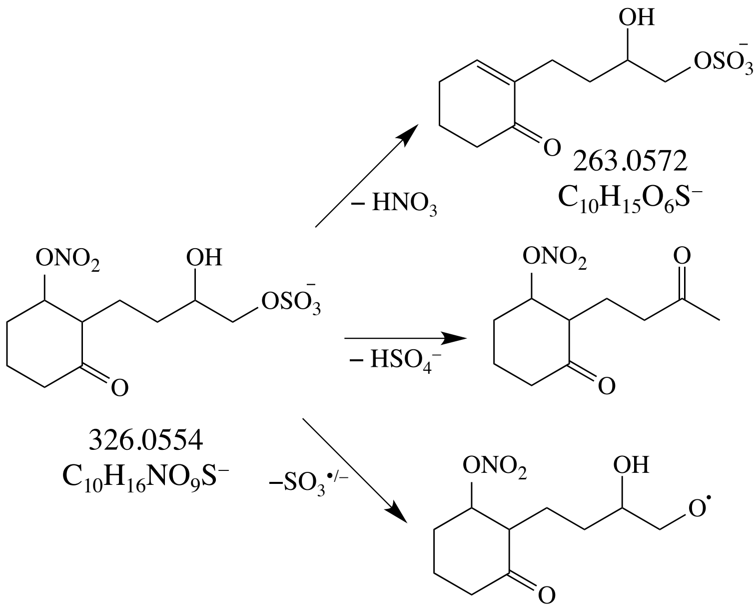


Figure S2. Fragmentation schemes for selected decalin-derived OSs: *a*) *m/z* 265.0752 ($C_{10}H_{17}O_6S^-$), (*b*) *m/z* 269.0696 ($C_9H_{17}O_7S^-$), (*c*) *m/z* 295.0494 ($C_{10}H_{15}O_8S^-$) and (*d*) *m/z* 326.0554 ($C_{10}H_{16}NO_9S^-$). MS^2 spectra are reported in Figure 2.

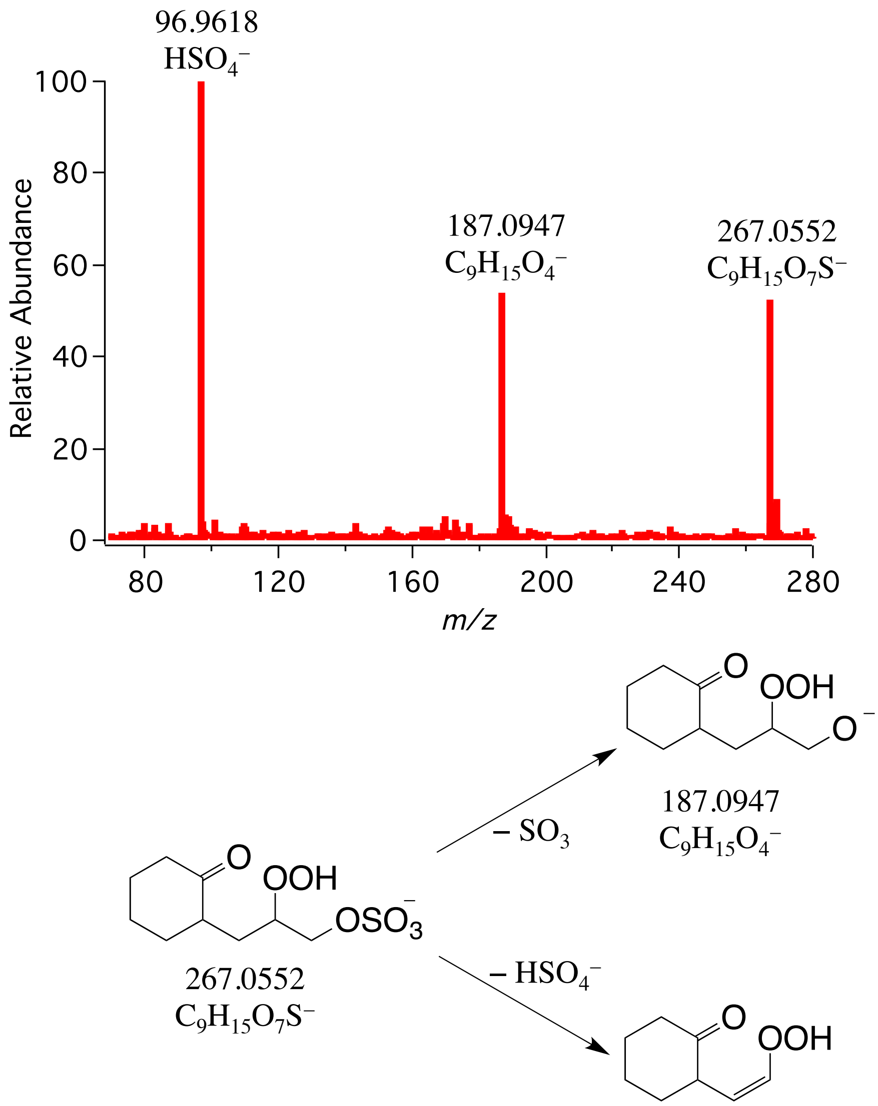


Figure S3. MS[2] spectrum and fragmentation scheme of ion at *m/z* 267.0552 identified in SOA formed from decalin oxidation.

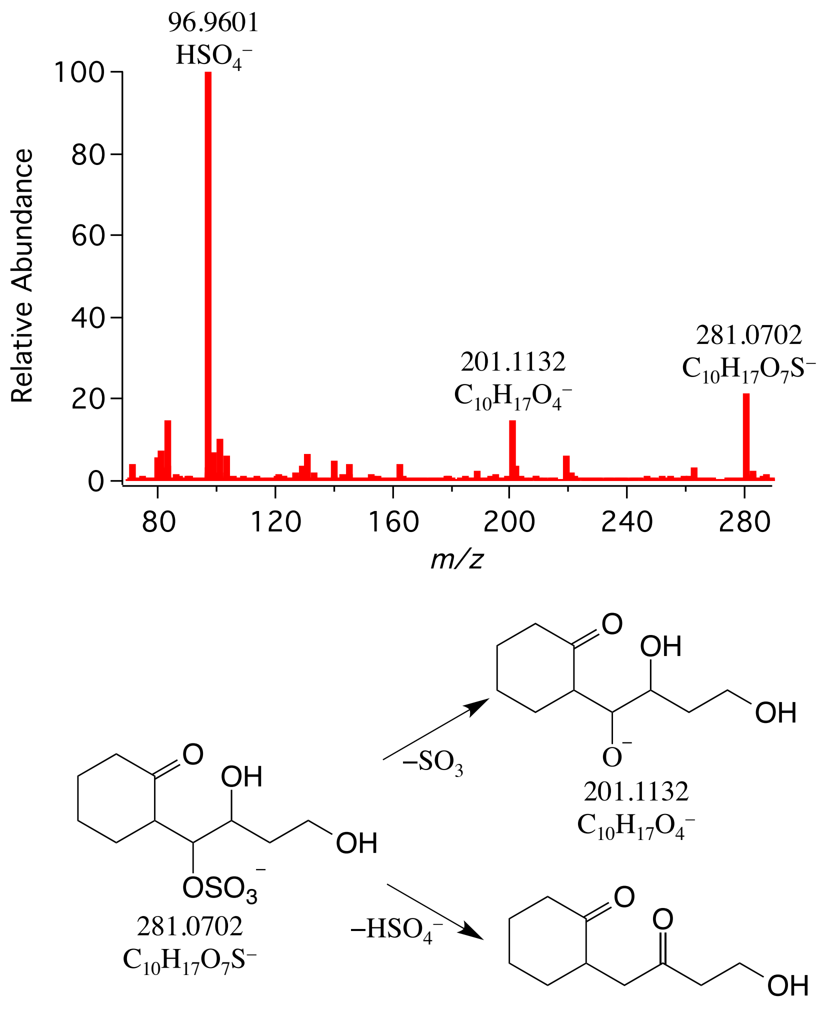


Figure S4. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 281.0702 identified in SOA formed from decalin oxidation.

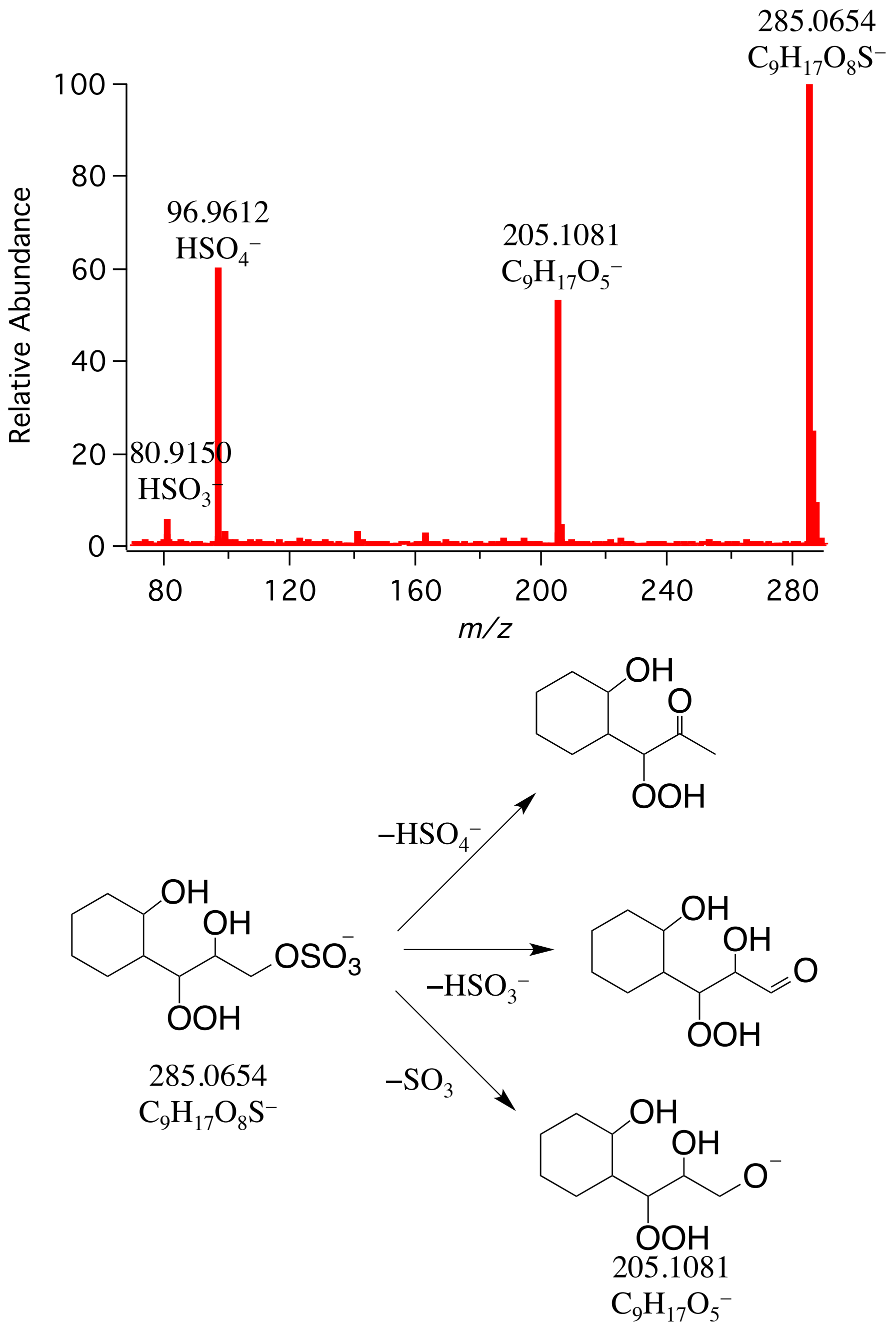
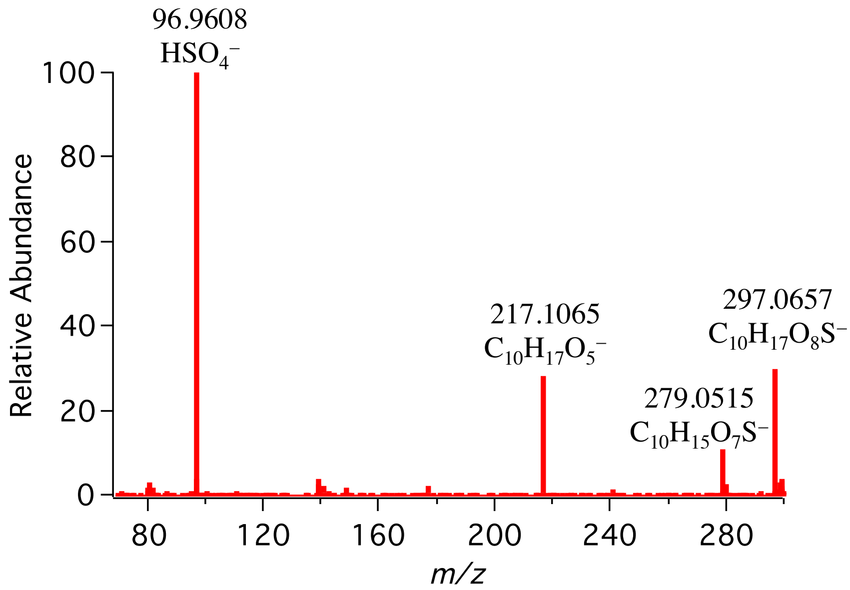


Figure S5. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 285.0654 identified in SOA formed from decalin oxidation.



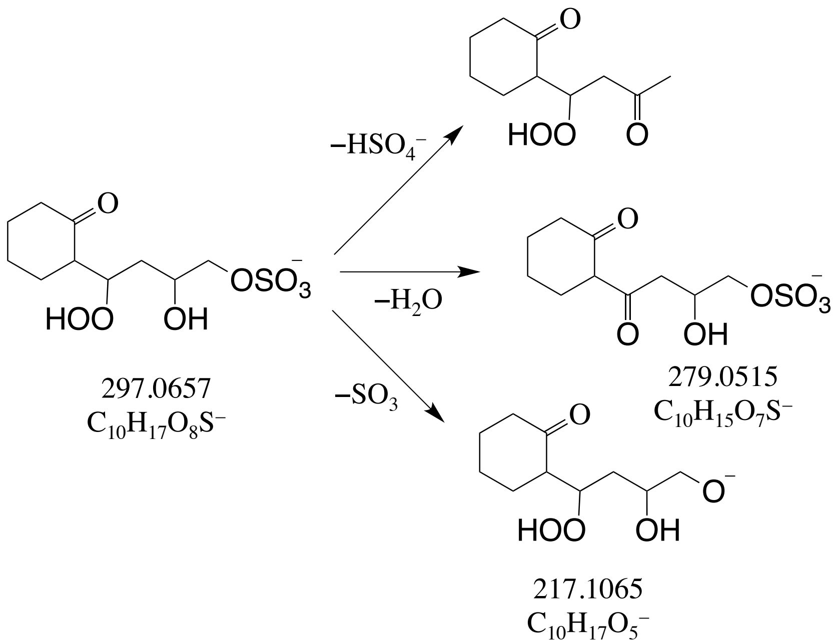


Figure S6. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 297.0669 identified in SOA formed from decalin oxidation.

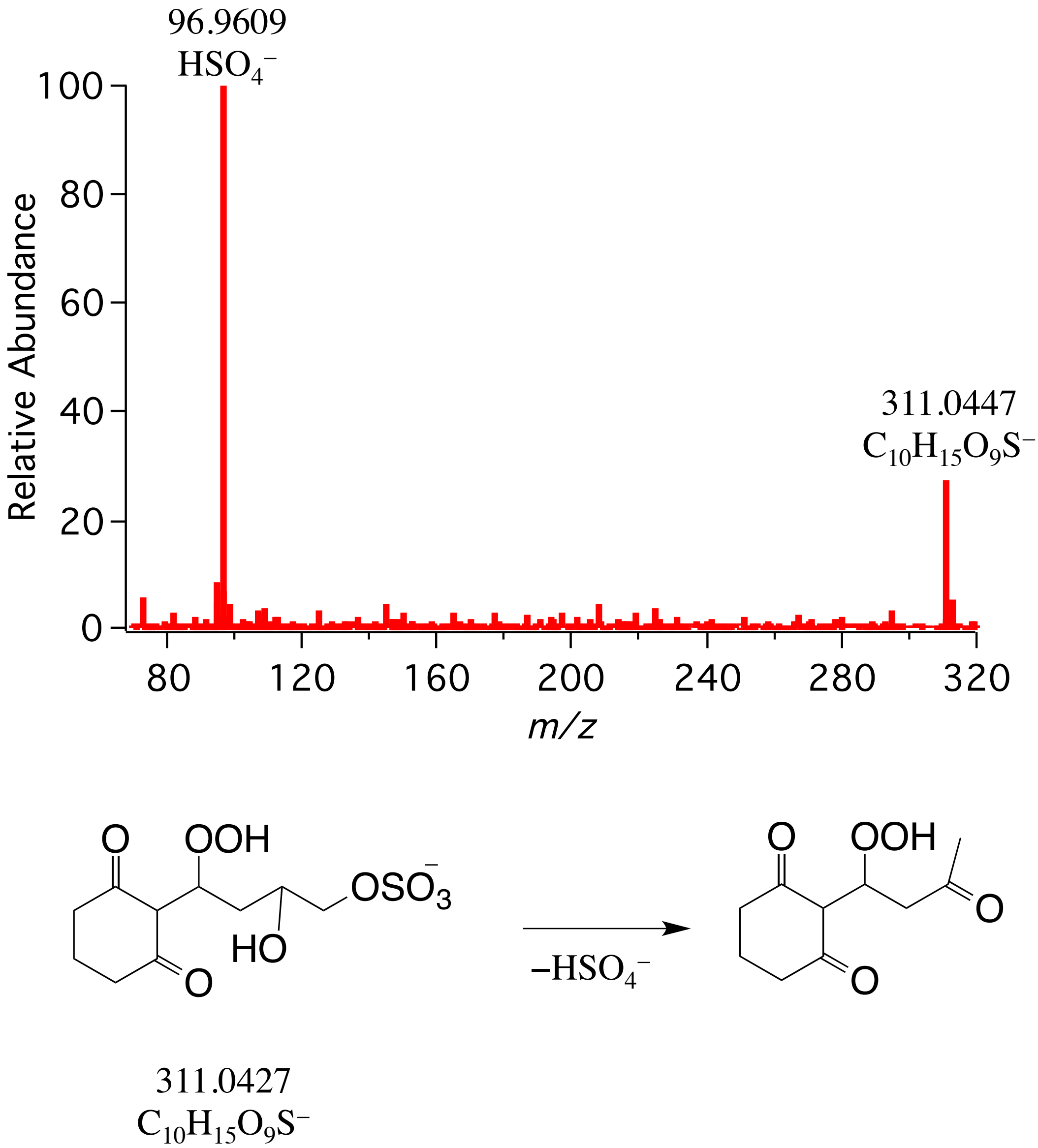


Figure S7. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 311.0427 identified in SOA formed from decalin oxidation.

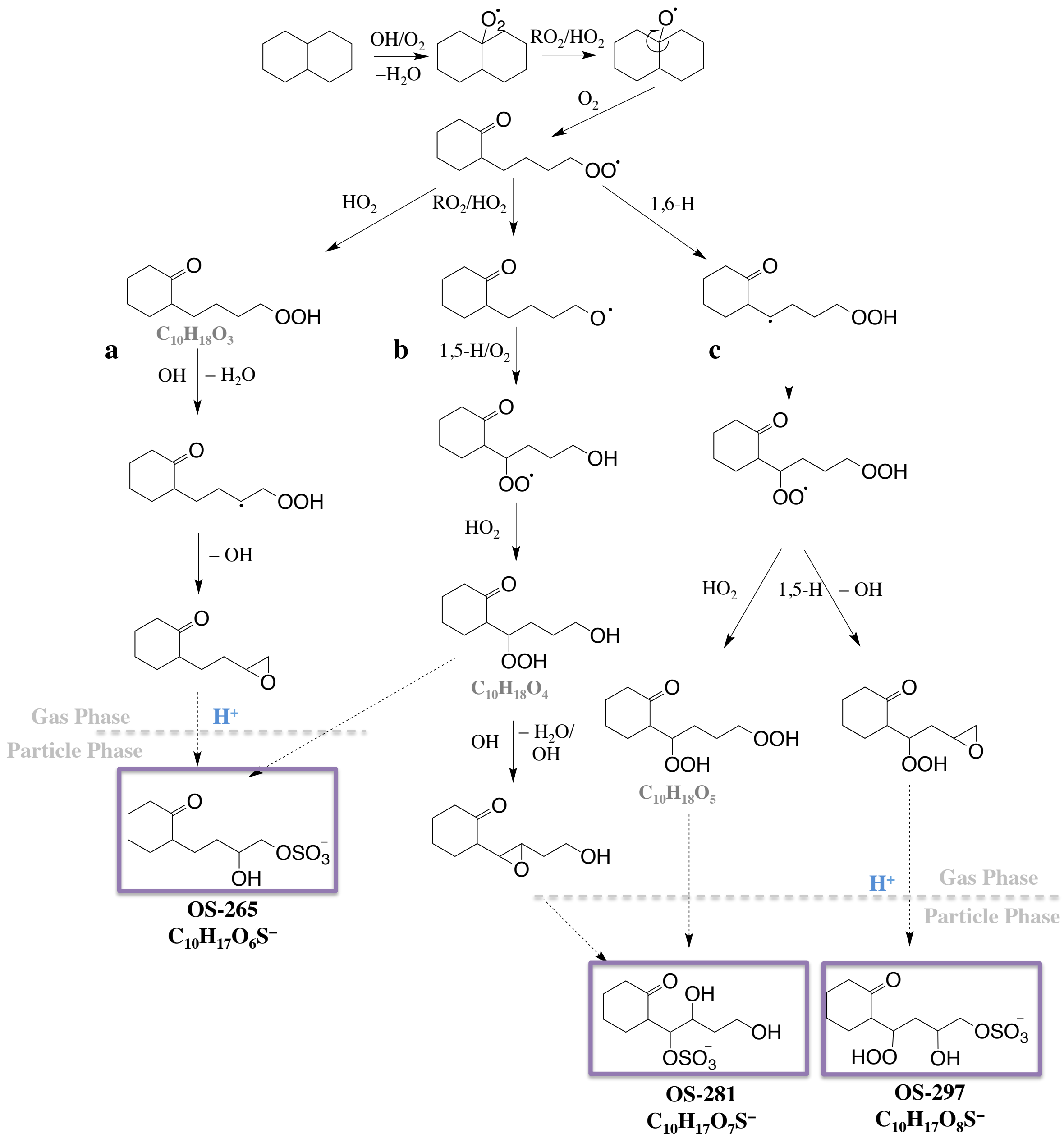


Figure S8. Tentatively proposed formation pathways of OS-265 (265.0752), OS-281 (281.0702) and OS-295 (295.0494) from the oxidation of decalin in the presence of ammonium sulfate aerosol.

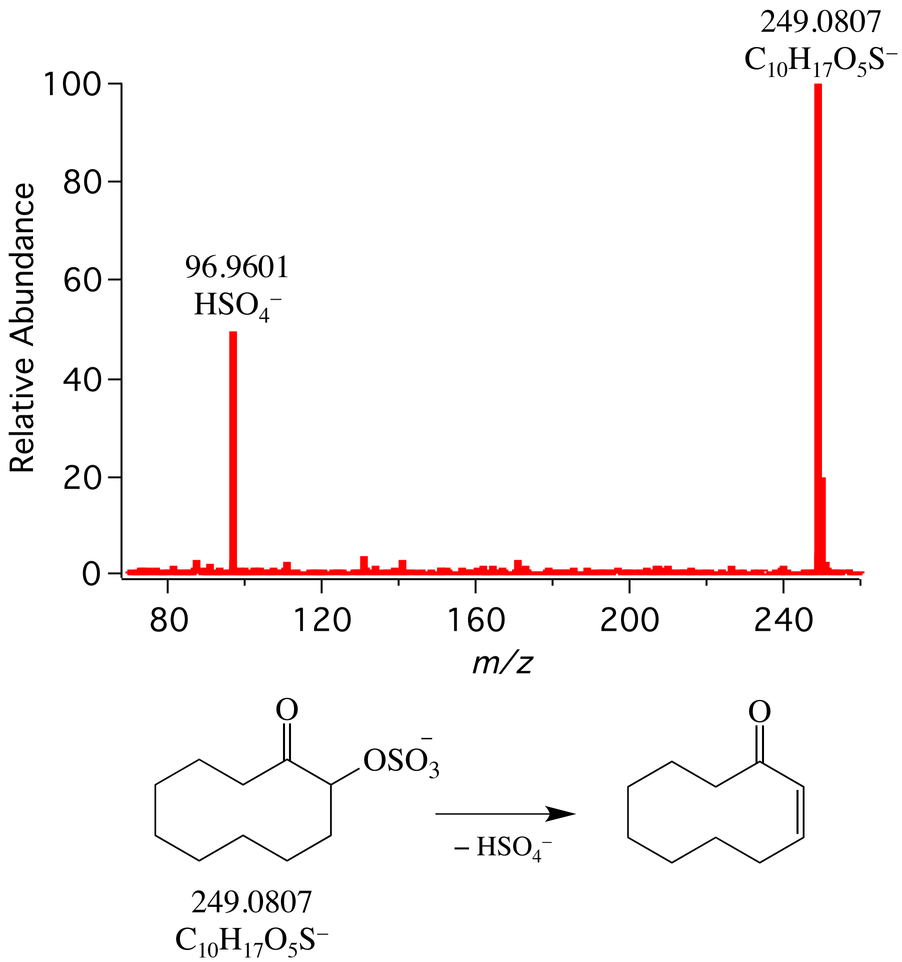


Figure S9. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 249.0807 identified in SOA formed from cyclodecane oxidation.

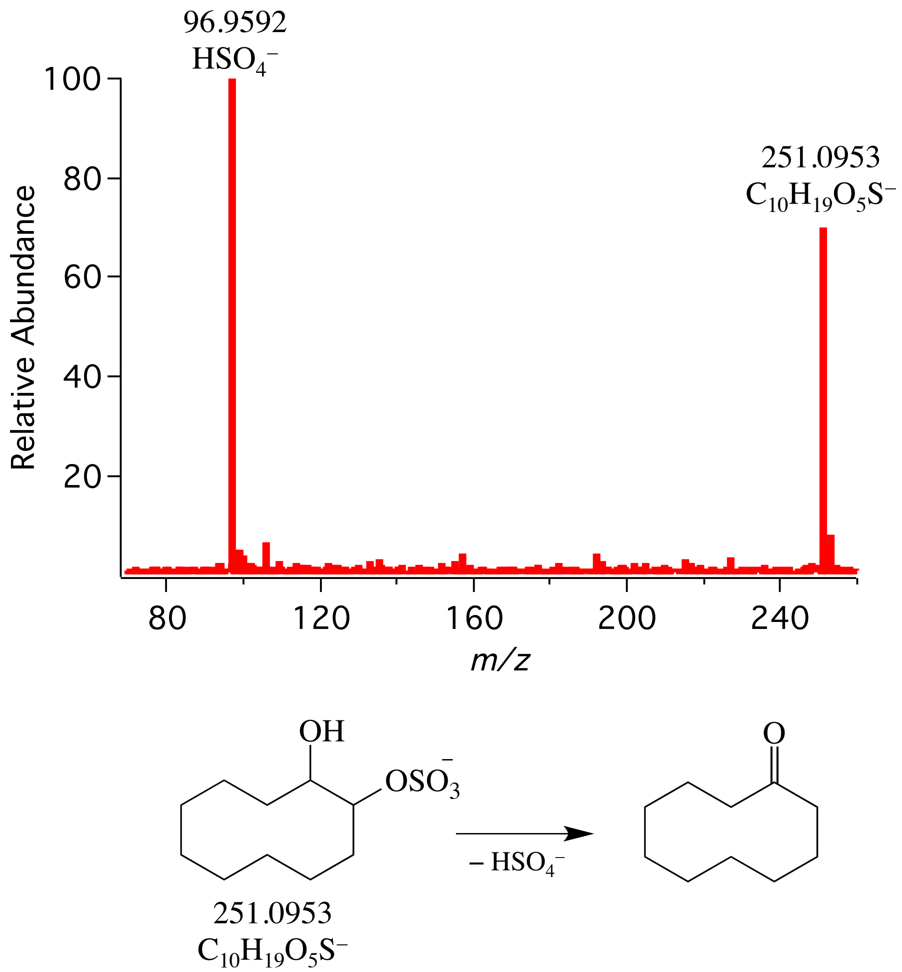


Figure S10. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 251.0953 identified in SOA formed from cyclodecane oxidation.

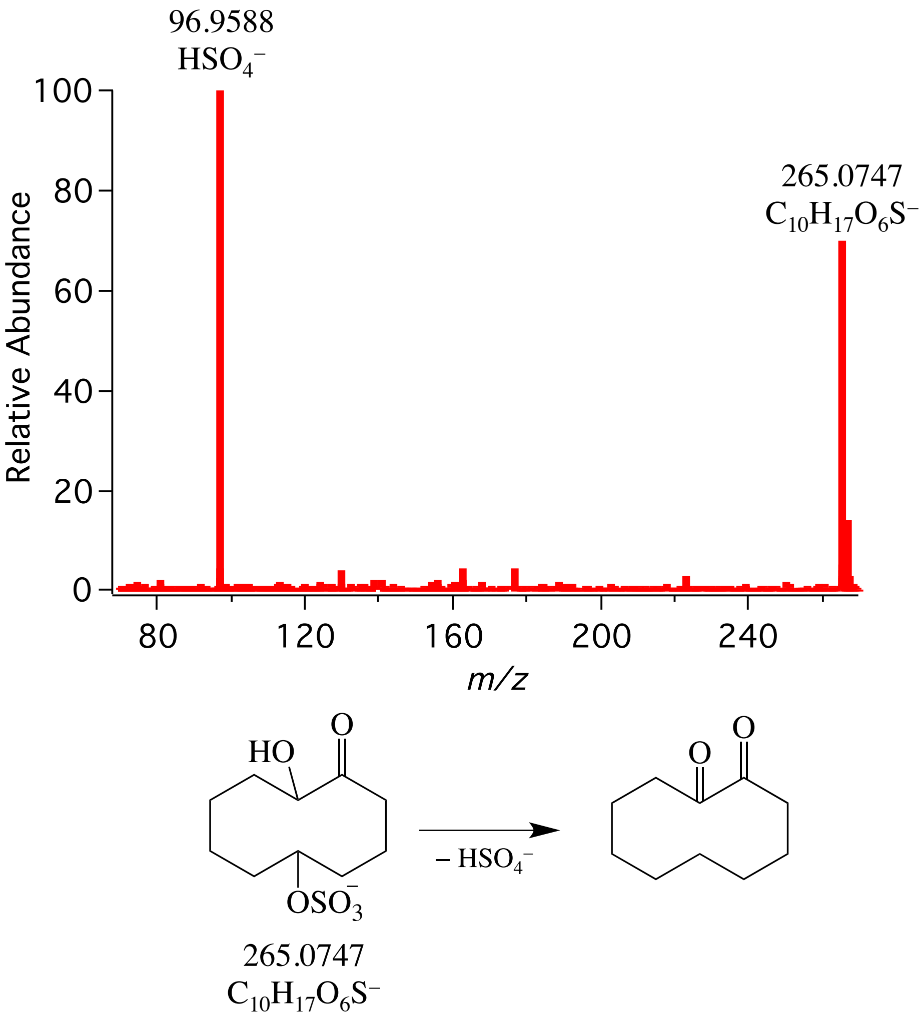


Figure S11. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 265.0747 identified in SOA formed from cyclodecane oxidation.

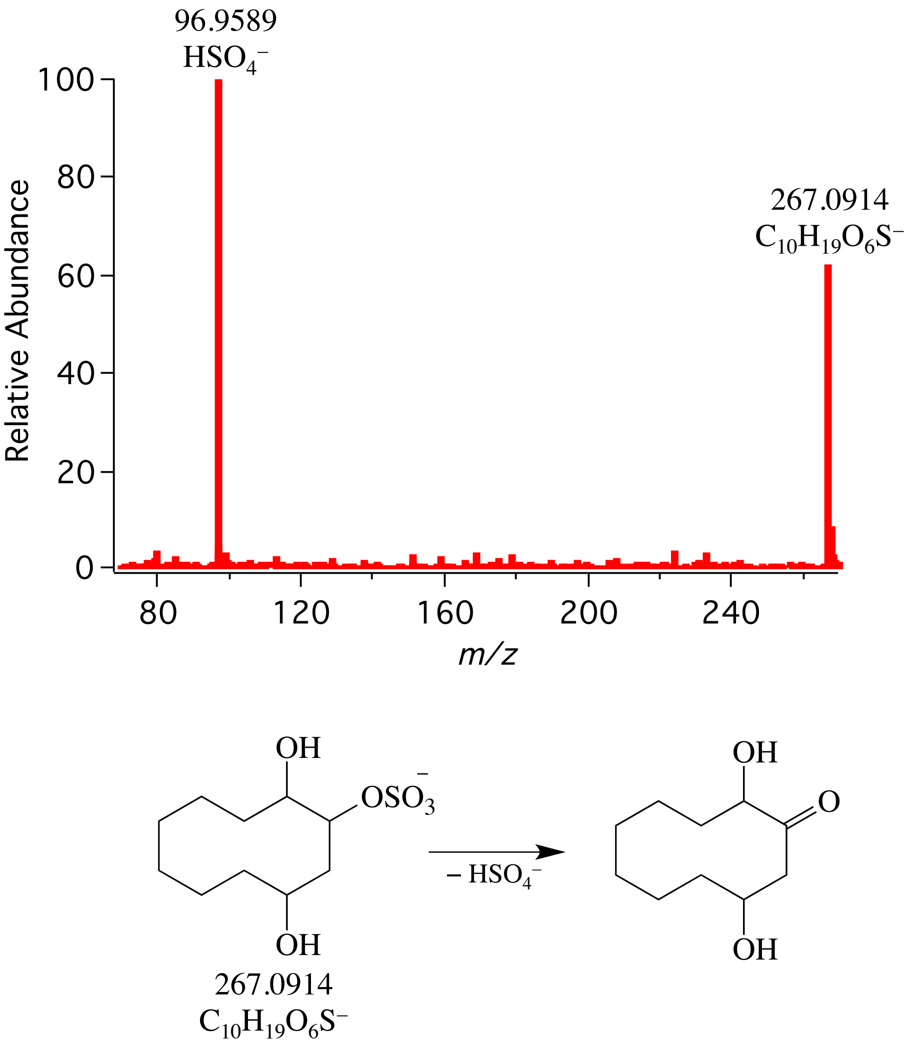


Figure S12. MS[2] spectrum and fragmentation scheme of the parent ion at *m*/*z* 267.0914 identified in SOA formed from cyclodecane oxidation.

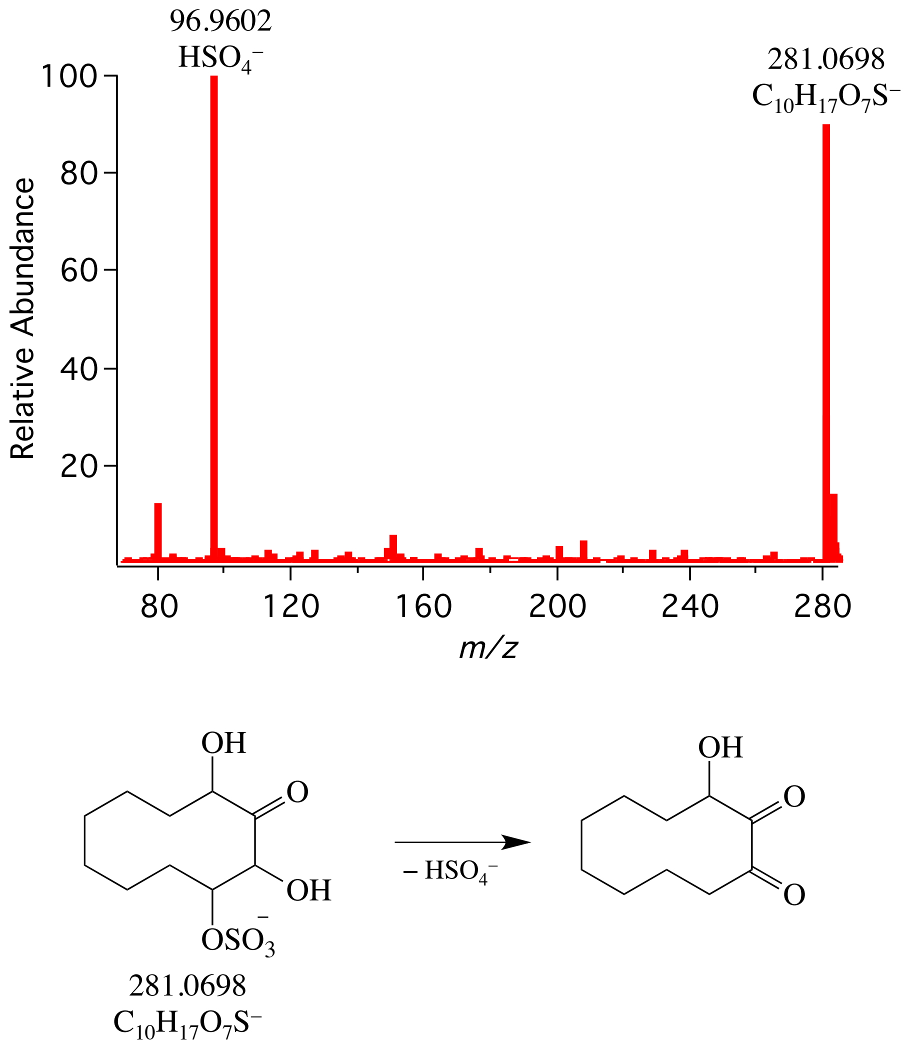


Figure S13. MS^2 spectrum and fragmentation scheme of the parent ion at *m/z* 281.0698 identified in SOA formed from cyclodecane oxidation.

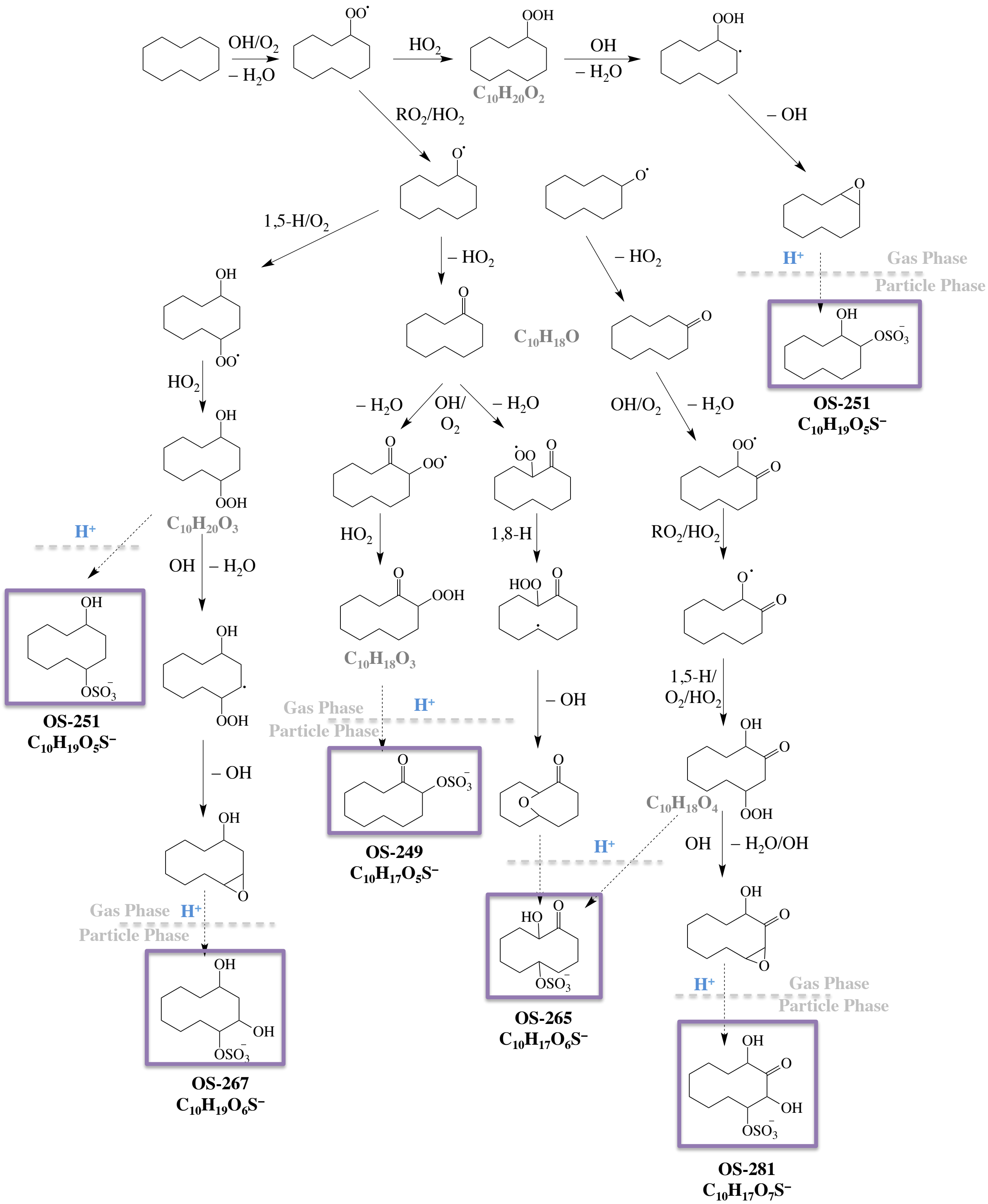


Figure S14. Tentatively proposed formation pathways of OSs formed from the oxidation of cyclodecane in presence of sulfate aerosol.

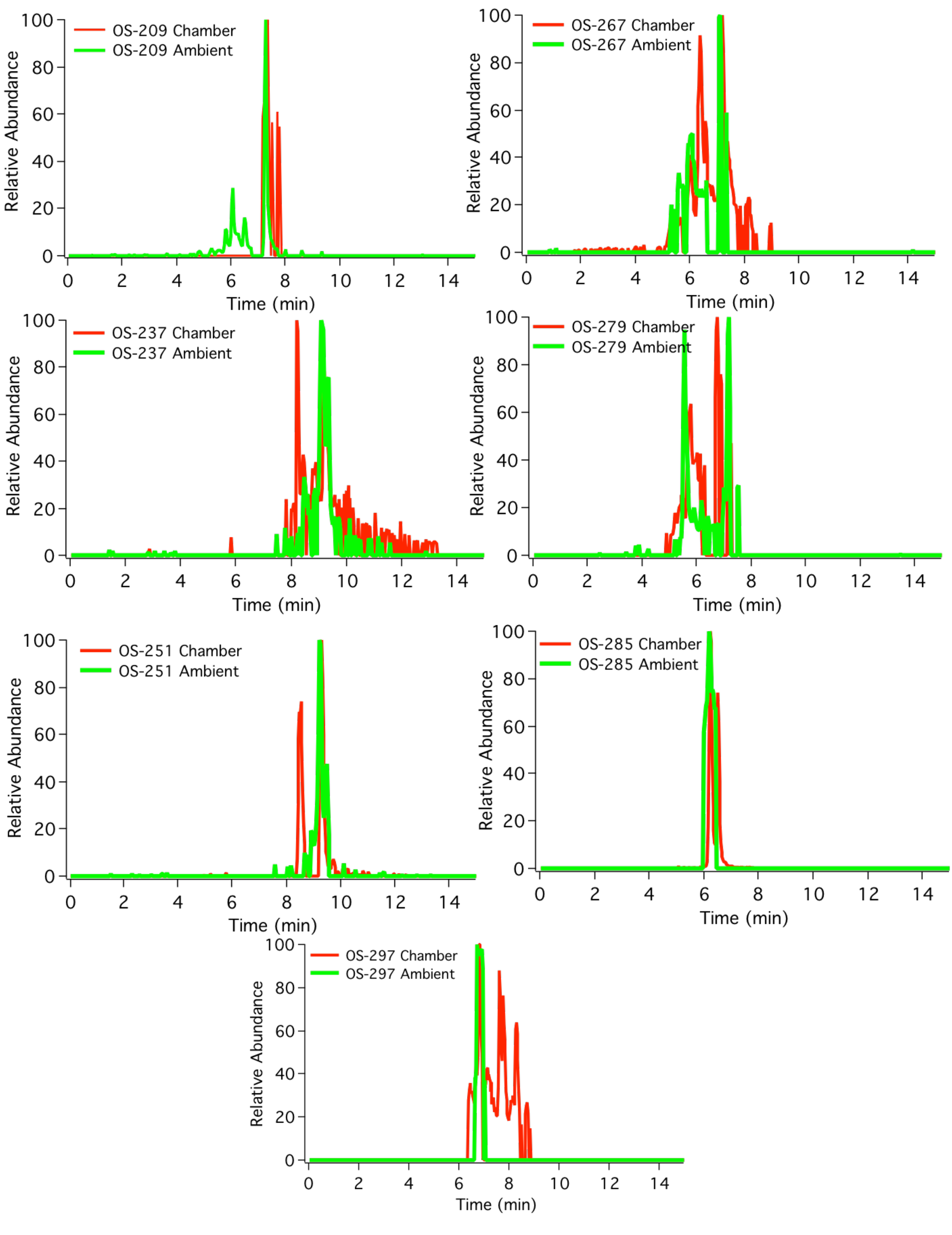


Figure S15. Extracted ion chromatograms (EICs) for alkane-derived OSs identified in aerosol collected from both smog chamber experiments (in red) and field studies (in green).