

Supporting information

Influence of Aerosol Acidity on the Chemical Composition of Secondary Organic Aerosol from β - caryophyllene

M. N. Chan¹, J. D. Surratt^{2*}, A. W. H. Chan^{2**}, K. Schilling², J. H. Offenberg³, M. Lewandowski³, E. O. Edney³, T. Kleindienst³, M. Jaoui⁴, E.S. Edgerton⁵, R. L. Tanner⁶, S. L. Shaw⁷, M. Zheng⁸, E. M. Knipping⁹, J.H. Seinfeld^{1,2}

¹Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California, USA.

²Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, USA.

³National Exposure Research Laboratory, Human Exposure Atmospheric Sciences Division, United States Environmental Protection Agency, Research Triangle Park, North Carolina, USA.

⁴Alion Science and Technology, P.O. Box 12313, Research Triangle Park, North Carolina, USA.

⁵Atmospheric Research and Analysis, Inc., Cary, North Carolina, USA.

⁶Environmental Technologies, Tennessee Valley Authority, Muscle Shoals, Alabama, USA.

⁷Electric Power Research Institute, Palo Alto, California, USA.

⁸School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA.

⁹Electric Power Research Institute, Washington, DC, USA.

*Present address: Department of Environmental Science and Engineering, University of North Carolina at Chapel Hill, North Carolina, USA

**Present address: Department of Environmental Science, Policy and Management, University of California, Berkeley, California, USA

To whom correspondence should be addressed: J.H. Seinfeld (seinfeld@caltech.edu)

Table S1. β -caryophyllene products observed both in the series of β -caryophyllene/NO_x irradiation experiments and in fine ambient aerosol collected in downtown Atlanta, GA (JST) and a rural location in Yorkville, GA (YRK) during the 2008 AMIGAS Campaign ^a

Compound	Sample	RT ^b (min)	[M+H] ⁺				[M+Na] ⁺				[M+CH ₃ OH+Na] ⁺				Concentration ^d	
			Formula	Measured mass	Theoretical mass	mDa	Formula	Measured mass	Theoretical mass	mDa	Formula	Measured mass	Theoretical mass	mDa		
β -nocyaryophyllon aldehyde (C ₁₄ H ₂₂ O ₃) 238(+)	Experiment 4	9.94	C ₁₄ H ₂₂ O ₃ ⁺	239.1632	239.1647	-1.5	C ₁₄ H ₂₂ O ₃ Na ⁺	261.1465	261.1467	-0.2	C ₁₅ H ₂₆ O ₄ Na ⁺	293.1719	293.1729	-1.0		
	JST 080908D	9.91		239.1658	239.1647	1.1		261.1490	261.1467	2.3		293.1734	293.1729	0.5	3.7	
	JST 080908N	9.90		239.1654	239.1647	0.7		261.1496	261.1467	2.9		293.1752	293.1729	2.3	5.3	
	JST 090608D	9.91		239.1656	239.1647	0.9		261.1495	261.1467	2.8		293.1723	293.1729	-0.6	2.7	
	JST 090608N	9.93		239.1642	239.1647	-0.5		261.1478	261.1467	1.1		293.1727	293.1729	-0.2	14	
	YRK 081208D	n.d.														
	YRK 081208N	n.d.														
	YRK 090608D	9.97		239.1670	239.1647	2.3		261.1476	261.1467	0.9		293.1734	293.1729	0.5	4.5	
	YRK 090608N	9.96		239.1674	239.1647	2.7		261.1432	261.1467	-3.5		293.1743	293.1729	1.4	20	
	β -hydroxynocyaryophyllon aldehyde (C ₁₄ H ₂₂ O ₄) 254a(+)	Experiment 4	9.78	C ₁₄ H ₂₂ O ₄ ⁺	255.1593	255.1596	-0.3	C ₁₄ H ₂₂ O ₄ Na ⁺	277.1374	277.1416	-4.2	C ₁₅ H ₂₆ O ₅ Na ⁺	309.1667	309.1678	-1.1	
JST 080908D		9.75		255.1613	255.1596	1.7		277.1424	277.1416	0.8		309.1671	309.1678	-0.7	2.5	
JST 080908N		9.76		255.1624	255.1596	2.8		277.1424	277.1416	0.8		309.1650	309.1678	-2.8	3.7	
JST 090608D		9.74		255.1619	255.1596	2.3		277.1422	277.1416	0.6		309.1713	309.1678	3.5	1.9	
JST 090608N		9.78		255.1603	255.1596	0.7		277.1431	277.1416	1.5		309.1707	309.1678	2.9	2.9	
YRK 081208D		9.76		255.1609	255.1596	1.3		277.1422	277.1416	0.6		309.1718	309.1678	4.0	8.1	
YRK 081208N		9.80		255.1637	255.1596	4.1		277.1435	277.1416	1.9		309.1708	309.1678	3.0	1.7	
YRK 090608D		9.80		255.1604	255.1596	0.8		277.1430	277.1416	1.4		309.1707	309.1678	2.9	2.9	
YRK 090608N		9.79		255.1609	255.1596	1.3		277.1426	277.1416	1.0		309.1699	309.1678	2.1	2.1	
C ₁₅ H ₂₂ O ₄ 268(+)		Experiment 4	9.44	C ₁₅ H ₂₂ O ₄ ⁺	269.1739	269.1753	-1.4	C ₁₅ H ₂₂ O ₄ Na ⁺	291.1525	291.1572	-4.7		n.d.			
		9.60		269.1746	269.1753	-0.7		291.1528	291.1572	-4.4		n.d.				
	JST 080908D	9.41		269.1721	269.1753	-3.2		291.1577	291.1572	0.5		n.d.			1.2	
		9.57		269.1739	269.1753	-1.4		291.1578	291.1572	0.6		n.d.			1.2	
	JST 080908N	9.40		269.1706	269.1753	-4.7		291.1565	291.1572	-0.7		n.d.			1.4	
		9.56		269.1717	269.1753	-3.6		291.1578	291.1572	0.6		n.d.			1.6	
	JST 090608D	9.40		269.1725	269.1753	-2.8		291.1578	291.1572	0.6		n.d.			1.3	
		9.56		269.1741	269.1753	-1.2		291.1561	291.1572	-1.1		n.d.			1.5	
	JST 090608N	9.42		269.1750	269.1753	-0.3		291.1581	291.1572	0.9		n.d.			1.1	
		9.59		269.1727	269.1753	-2.6		291.1575	291.1572	0.3		n.d.			1.5	
	YRK 081208D	9.42		269.1737	269.1753	-1.6		291.1548	291.1572	-2.4		n.d.			1.8	
		9.59		269.1740	269.1753	-1.3		291.1578	291.1572	0.6		n.d.			1.3	
	YRK 081208N	9.46		269.1749	269.1753	-0.4		291.1591	291.1572	1.9		n.d.			1.1	
		9.61		269.1769	269.1753	1.6		291.1577	291.1572	0.5		n.d.			1.2	
	YRK 090608D	9.45		269.1751	269.1753	-0.2		291.1577	291.1572	0.5		n.d.			2.0	
	9.61		269.1738	269.1753	-1.5		291.1569	291.1572	-0.3		n.d.			2.0		
YRK 090608N	9.45		269.1747	269.1753	-0.6		291.1578	291.1572	0.6		n.d.			1.8		
	9.61		269.1755	269.1753	0.2		291.1567	291.1572	-0.5		n.d.			1.6		
β -dihydroxynocyaryophyllon aldehyde (C ₁₄ H ₂₂ O ₅) ⁺ 270(+)	Experiment 4	9.23	C ₁₄ H ₂₂ O ₅ ⁺	271.1501	271.1545	-4.4	C ₁₄ H ₂₂ O ₅ Na ⁺	293.1348	293.1365	-1.7	C ₁₅ H ₂₆ O ₆ Na ⁺	325.1674	325.1627	4.7		
	JST 080908D	9.20		271.1549	271.1545	0.4		293.1395	293.1365	3		325.1645	325.1627	1.8	0.6	
	JST 080908N	n.d.														
	JST 090608D	9.21		271.1561	271.1545	1.6		293.1406	293.1365	4.1		325.1652	325.1627	2.5	0.7	
	JST 090608N	n.d.														
	YRK 081208D	9.22		271.1570	271.1545	2.5		293.1408	293.1365	4.3		325.1650	325.1627	2.3	1.1	
	YRK 081208N	9.26		271.1571	271.1545	2.6		293.1415	293.1365	5.0		325.1646	325.1627	1.9	0.6	
	YRK 090608D	9.25		271.1548	271.1545	0.3		293.1408	293.1365	4.3		325.1655	325.1627	2.8	0.5	
YRK 090608N	n.d.															

n.d. = adduct ions are not detected; ^a Day (10 a.m. to 6 p.m., local time) and night (10 p.m. to 6 a.m., local time); ^b RT = retention time; ^c Weak signal intensity observed for ambient samples; GF 14 sample is chosen as an example; ^d Concentration is expressed in term of the intensity of ion normalized by the sampling air volume (ion intensity/m³) in the AMIGAS samples.

Table S2. UPLC/ESI-TOFMS data for compounds detected by ESI in the positive ion mode in the series of β -caryophyllene/ NO_x irradiation experiments. Data are obtained from Experiment 4.

ESI(+) compound (name)	Suggested chemical formula	Retention time (min)	[M+H] ⁺ Measured mass	[M+H] ⁺ Theoretical mass	Error (mDa)	[M+Na] ⁺ Measured mass	[M+Na] ⁺ Theoretical mass	Error (mDa)	[M+CH ₃ +OH+Na] ⁺ Measured mass	[M+CH ₃ +OH+Na] ⁺ Theoretical mass	Error (mDa)
184(+)	C ₁₀ H ₂₆ O ₃	7.37	185.1173	185.1178	-0.5	207.0994	207.0997	-0.3	-		
238(+) (β -nocaryophyllon aldehyde)	C ₁₄ H ₂₂ O ₃	9.94	239.1632	239.1647	-1.5	261.1465	261.1467	-0.2	293.1719	293.1729	-1.0
250(+) (β -oxocaryophyllon aldehyde)	C ₁₅ H ₂₂ O ₃	9.63	251.1644	251.1647	-0.3	273.1465	273.1467	-0.2	-		
252a(+) (β -oxonocaryophyllon aldehyde)	C ₁₄ H ₂₀ O ₄	8.84	253.1416	253.1440	-2.4	275.1245	275.1259	-1.4	307.1545	307.1521	2.4
252b(+) (β -hydroxycaryophyllon aldehyde)	C ₁₅ H ₂₄ O ₃	10.41	253.1796	253.1804	-0.8	-			307.1841	307.1885	-4.4
		10.60	253.1784	253.1804	-2.0	-			307.1843	307.1885	-4.2
		10.71	253.1789	253.1804	-1.5	-			307.1844	307.1885	-4.1
N253(+)	C ₁₄ H ₂₃ NO ₃	8.47	254.1764	254.1756	0.8	276.1583	276.1576	0.7	-		
254a(+) (β -hydroxynocaryophyllon aldehyde)	C ₁₄ H ₂₂ O ₄	9.13	255.1574	255.1596	-2.2	277.1400	277.1416	-1.6	309.1686	309.1678	0.8
		9.78	255.1593	255.1596	-0.3	277.1374	277.1416	-4.2	309.1667	309.1678	-1.1
		10.22	255.1560	255.1596	-3.6	277.1403	277.1416	-1.3	309.1723	309.1678	4.5
254b(+)	C ₁₅ H ₂₆ O ₃	10.82	-			277.1790	277.1780	1.0	-		
N267(+)	C ₁₅ H ₂₅ NO ₃	6.80	268.1931	268.1913	1.8	290.1742	290.1732	1.0	-		
268(+)	C ₁₅ H ₂₄ O ₄	9.44	269.1739	269.1753	-1.4	291.1525	291.1572	-4.7	-		
		9.60	269.1746	269.1753	-0.7	291.1528	291.1572	-4.4	-		
270(+) (β -dihydroxynocaryophyllon aldehyde)	C ₁₄ H ₂₂ O ₅	9.23	271.1501	271.1545	-4.4	293.1348	293.1365	-1.7	325.1674	325.1627	4.7
298(+)	C ₁₅ H ₂₂ O ₆	7.58	299.1479	299.1495	-1.6	321.1315	321.1314	0.1	-		

Table S3. UPLC/ESI-TOFMS data for compounds detected by ESI in the negative ion mode in the series of β -caryophyllene/ NO_x irradiation experiments. Data are obtained from Experiment 4.

ESI(-) compound	Name	Suggested chemical formula	Retention time (min)	[M-H] ⁻ Measured mass	[M-H] ⁻ Theoretical mass	Error (mDa)
186(-)		$\text{C}_9\text{H}_{14}\text{O}_4$	6.23	185.0790	185.0814	-2.4
			6.56	185.0786	185.0814	-2.8
216(-)		$\text{C}_{10}\text{H}_{16}\text{O}_5$	6.32	215.0912	215.0919	-0.7
252a(-)		$\text{C}_{14}\text{H}_{20}\text{O}_4$	8.50	251.1272	251.1283	-1.1
252b(-)	β -caryophyllonic acid	$\text{C}_{15}\text{H}_{24}\text{O}_3$	10.03	251.1647	251.1647	0.0
254(-)	β -nocaryophyllonic acid / β -caryophyllinic acid	$\text{C}_{14}\text{H}_{22}\text{O}_4$	8.72	253.1407	253.1440	-3.3
			9.75	253.1417	253.1440	-2.3
256a(-)	β -hydroxynocaryophyllonic acid	$\text{C}_{13}\text{H}_{20}\text{O}_5$	7.94	255.1232	255.1232	0.0
			8.36	255.1219	255.1232	-1.3
256b(-)	Hydrated β -nocaryophyllonic acid	$\text{C}_{14}\text{H}_{24}\text{O}_4$	9.52	255.1603	255.1596	0.7
266(-)	β -oxocaryophyllonic acid	$\text{C}_{15}\text{H}_{22}\text{O}_4$	9.07	265.1462	265.1440	2.2
268a(-)	β -oxonocaryophyllonic acid	$\text{C}_{14}\text{H}_{20}\text{O}_5$	8.43	267.1229	267.1232	-0.3
			9.01	267.1238	267.1232	0.6
268b(-)	β -hydroxycaryophyllonic acid	$\text{C}_{15}\text{H}_{24}\text{O}_4$	9.11	267.1590	267.1596	-0.6
			9.47	267.1619	267.1596	2.3
270a(-)	β -hydroxynocaryophyllonic acid	$\text{C}_{14}\text{H}_{22}\text{O}_5$	8.17	269.1385	269.1389	-0.4
			8.28	269.1377	269.1389	-1.2
270b(-)	Hydrated β -caryophyllonic acid	$\text{C}_{15}\text{H}_{26}\text{O}_4$	9.05	269.1737	269.1753	-1.6
272(-)	Hydrated β -nocaryophyllonic acid	$\text{C}_{14}\text{H}_{24}\text{O}_5$	7.92	271.1540	271.1545	-0.5
284(-)	Hydrated β -oxocaryophyllonic acid	$\text{C}_{15}\text{H}_{24}\text{O}_5$	8.09	283.1531	283.1545	-1.4
			8.98	283.1534	283.1545	-1.1

Table S3 (Continued). UPLC/ESI-TOFMS data for compounds detected by ESI in the negative ion mode in the series of β -caryophyllene/ NO_x irradiation experiments. Data are obtained from Experiment 4.

ESI(-) compound	Name	Suggested chemical formula	Retention time (min)	[M-H] ⁻ Measured mass	[M-H] ⁻ Theoretical mass	Error (mDa)
286a(-)	β -dihydroxynocaryophyllonic acid	$\text{C}_{14}\text{H}_{22}\text{O}_6$	8.06	285.1347	285.1338	0.9
			8.34	285.1339	285.1338	0.1
286b(-)	Hydrated β -hydroxycaryophyllonic acid	$\text{C}_{15}\text{H}_{26}\text{O}_5$	9.23	285.1691	285.1702	-1.1
			9.3	285.1687	285.1702	-1.5
294(-)		$\text{C}_{17}\text{H}_{26}\text{O}_4$	9.99	293.1771	293.1753	1.8
312(-)		$\text{C}_{13}\text{H}_{28}\text{O}_8$	10.34	311.1691	311.1706	-1.5
			10.49	311.1692	311.1706	-1.4
314a(-)		$\text{C}_{15}\text{H}_{22}\text{O}_7$	7.05	313.1300	313.1287	1.3
314b(-)		$\text{C}_{16}\text{H}_{26}\text{O}_6$	8.24	313.1642	313.1651	-0.9
			8.72	313.1635	313.1651	-1.6
			8.98	313.1641	313.1651	-1.0
			9.12	313.1643	313.1651	-0.8
320(-)		$\text{C}_{14}\text{H}_{24}\text{O}_8$	10.07	319.1440	319.1393	4.7
328(-)		$\text{C}_{17}\text{H}_{28}\text{O}_6$	8.44	327.1802	327.1808	-0.6
			8.58	327.1790	327.1808	-1.8
330a(-)		$\text{C}_{16}\text{H}_{26}\text{O}_7$	6.97	329.1596	329.1600	-0.4
			7.02	329.1606	329.1600	0.6
			8.29	329.1599	329.1600	0.1
330b(-)		$\text{C}_{17}\text{H}_{30}\text{O}_6$	8.82	329.1966	329.1964	0.2
			8.89	329.1927	329.1964	-3.7
			9.05	329.1971	329.1964	0.7

Table S4. UPLC/ESI-TOFMS data for compounds detected by ESI in the negative ion mode in the series of β -caryophyllene/ NO_x irradiation experiments (nitrogen-containing compounds). Data are obtained from Experiment 4.

ESI(-) compound	Suggested chemical formula	Retention time (min)	[M-H] ⁻ Measured mass	[M-H] ⁻ Theoretical mass	Error (mDa)
N195(-)	$\text{C}_{10}\text{H}_{13}\text{NO}_3$	10.15	194.0805	194.0817	-1.2
N345(-)	$\text{C}_{16}\text{H}_{27}\text{NO}_7$	9.64	344.1692	344.1709	-1.7
		9.7	344.1715	344.1709	0.6
N347(-)	$\text{C}_{15}\text{H}_{25}\text{NO}_8$	9.03	346.1506	346.1502	-1.7
		9.19	346.1510	346.1502	0.8
		9.27	346.1493	346.1502	-0.9
N349a(-)	$\text{C}_{14}\text{H}_{23}\text{NO}_9$	9.37	348.1299	348.1295	0.4
N349b(-)	$\text{C}_{15}\text{H}_{27}\text{NO}_8$	9.83	348.1674	348.1658	1.6
		9.89	348.1672	348.1658	1.4
N350(-)	$\text{C}_{13}\text{H}_{22}\text{N}_2\text{O}_9$	8.63	349.1246	349.1247	0.1
		8.93	349.1251	349.1247	0.4
N363a(-)	$\text{C}_{15}\text{H}_{25}\text{NO}_9$	8.38	362.1455	362.1451	0.4
		8.87	362.1445	362.1451	-0.6
		9.12	362.1456	362.1451	0.5
N363b(-)	$\text{C}_{16}\text{H}_{29}\text{NO}_8$	9.47	362.1808	362.1815	-0.7
		10.23	362.1785	362.1815	-3.0
N375(-)	$\text{C}_{17}\text{H}_{29}\text{NO}_8$	9.17	374.1814	374.1815	-0.1
		9.8	374.1819	374.1815	0.4
		9.9	374.1846	374.1815	3.1
N546(-)	$\text{C}_{24}\text{H}_{38}\text{N}_2\text{O}_{12}$	9.35	545.2341	545.2347	-0.6
	$\text{C}_{12}\text{H}_{19}\text{NO}_6$ (monomer)		272.1109	272.1134	-2.5

Table S5. UPLC/ESI-TOFMS data for compounds detected by ESI in the negative ion mode in the series of β -caryophyllene/ NO_x irradiation experiments (organosulfates). Data are obtained from Experiment 4.

ESI(-) compound	Suggested chemical formula	Retention time (min)	[M-H] ⁻ Measured mass	[M-H] ⁻ Theoretical mass	Error (mDa)
S252(-)	$\text{C}_9\text{H}_{16}\text{O}_6\text{S}$	7.12	251.0592	251.0589	-0.3
S304(-)	$\text{C}_{14}\text{H}_{24}\text{O}_5\text{S}$	9.52	303.1267	303.1266	0.1
		9.73	303.1273	303.1266	0.7
S318(-)	$\text{C}_{15}\text{H}_{26}\text{O}_5\text{S}$	9.8	317.1433	317.1423	1.0
		10.07	317.1414	317.1423	-0.9
S320(-)	$\text{C}_{14}\text{H}_{24}\text{O}_6\text{S}$	8.13	319.1204	319.1215	-1.1
		8.67	319.1223	319.1215	0.8
		9.05	319.1229	319.1215	1.4
S334a(-)	$\text{C}_{14}\text{H}_{22}\text{O}_7\text{S}$	7.42	333.0998	333.1008	-1.0
S334b(-)	$\text{C}_{15}\text{H}_{26}\text{O}_6\text{S}$	8.62	333.1360	333.1372	-1.2
		8.72	333.1371	333.1372	-0.1
S348(-)	$\text{C}_{15}\text{H}_{24}\text{O}_7\text{S}$	7.62	347.1158	347.1165	-0.7
		7.83	347.1141	347.1165	-2.4
		8.05	347.1176	347.1165	1.1
S350a(-)	$\text{C}_{14}\text{H}_{22}\text{O}_8\text{S}$	7.74	349.0969	349.0957	1.2
		8.63	349.0960	349.0957	0.3
		8.93	349.0967	349.0957	1.0
		9.93	349.0962	349.0957	0.5
S350b(-)	$\text{C}_{15}\text{H}_{26}\text{O}_7\text{S}$	7.82	349.1332	349.1321	1.1
		8.43	349.1333	349.1321	1.2
		8.64	349.1308	349.1321	-1.3
S352(-)	$\text{C}_{14}\text{H}_{24}\text{O}_8\text{S}$	6.58	351.1117	351.1114	0.3
		6.77	351.1113	351.1114	-0.1
		6.85	351.1114	351.1114	0.0

Table S5 (Continued). UPLC/ESI-TOFMS data for compounds detected by ESI in the negative ion mode in the series of β -caryophyllene/ NO_x irradiation experiments (organosulfates). Data are obtained from Experiment 4.

ESI(-) compound	Suggested chemical formula	Retention time (min)	[M-H] ⁻ Measured mass	[M-H] ⁻ Theoretical mass	Error (mDa)
S364a(-)	$\text{C}_{15}\text{H}_{24}\text{O}_8\text{S}$	7.34	363.1126	363.1114	1.2
S364b(-)	$\text{C}_{16}\text{H}_{28}\text{O}_7\text{S}$	8.29	363.1481	363.1478	0.3
		8.67	363.1471	363.1478	-0.7
		8.82	363.1483	363.1478	0.5
		8.89	363.1473	363.1478	-0.5
		9.06	363.1468	363.1478	-1.0
S380(-)	$\text{C}_{16}\text{H}_{28}\text{O}_8\text{S}$	8.38	379.1429	379.1427	0.2
Nitrated Organosulfates					
S363(-)	$\text{C}_{15}\text{H}_{25}\text{NO}_7\text{S}$	7.34	362.1302	362.1273	2.9
S383(-)	$\text{C}_{14}\text{H}_{25}\text{NO}_9\text{S}$	8.83	382.1162	382.1172	-1.0
		9.13	382.1178	382.1172	0.6
		9.94	382.1189	382.1172	1.7
		10.03	382.1193	382.1172	2.1