Supplement of Atmos. Chem. Phys., 15, 5683–5695, 2015
http://www.atmos-chem-phys.net/15/5683/2015/
doi:10.5194/acp-15-5683-2015-supplement


Atmospheric Chemistry and Physics Open Access

*Supplement of*

# Molecular composition of fresh and aged secondary organic aerosol from a mixture of biogenic volatile compounds: a high-resolution mass spectrometry study

**I. Kourtchev et al.**

*Correspondence to:* I. Kourtchev (ink22@cam.ac.uk) and M. Kalberer (mk594@cam.ac.uk)

Table S1. Tentative assignments of the major LC/MS peaks in SOA from dark ozonolysis of the BVOC mixture containing *α*-, *β*-pinene, $\Delta_3$-carene and isoprene.

| **Retention time, min** | **Measured [M-1]$^-$** | **Molecular formula** | **Tentative assignment[ref]** | **Source** |
|---|---|---|---|---|
| | | | ***monomers*** | |
| 19.2 | 187.06097 | $C_8H_{12}O_5$ | unknown terpenoic acid[1,2] | *α-, β*-pinene |
| 21.17 | 157.05040 | $C_7H_9O_4$ | terebic acid[1,2,3] | *α, β*-pinene, $\Delta_3$-carene |
| 22.9 | 171.06609 | $C_8H_{12}O_4$ | terpenylic acid[1,2,3] | *α, β*-pinene, $\Delta_3$-carene |
| 24.14 | 203.05582 | $C_8H_{12}O_6$ | MBTCA[2,3,4,5] | α-pinene |
| 25.98 | 185.08191 | $C_9H_{14}O_4$ | homoterpenylic acid[1,2,3] | *α, β*-pinene, $\Delta_3$-carene |
| 26.7 | 215.09230 | $C_{10}H_{16}O_5$ | Unknown[2,6] | *α*-pinene |
| 29.43 | 231.08711 | $C_{10}H_{16}O_6$ | diaterpenylic acid acetate (DTA)[2,3] | *α-, β*-pinene |
| 30.38 | 185.08167 | $C_9H_{14}O_4$ | *cis*-pinic acid[2,3,7,8,9] | *α-, β*-pinene |
| 32.58 | 185.08168 | $C_9H_{14}O_4$ | *cis*-caric acid[2,3] | *α, β*-pinene, $\Delta_3$-carene |
| 33.34 | 169.08710 | $C_9H_{14}O_3$ | 3-norcaronic acid[2,7] | $\Delta_3$-carene |
| 34.05 | 183.10248 | $C_{10}H_{16}O_3$ | *cis*-pinonic acid[1,2,3,10] | *α-, β*-pinene |
| 36.46 | 187.09731 | $C_9H_{16}O_4$ | 2-hydroxyterpenylic acid[2,3] | *α-, β*-pinene |
| | | | ***Dimers*** | |
| 35.12 | 343.13983 | $C_{16}H_{23}O_8$ | Pinyl-diaterebyl ester MW 344[11,12,13] | *α, β*-pinene |
| 37.42 | 357.15509 | $C_{17}H_{26}O_8$ | Pinyl-diaterpenyl ester MW 358[11,12,13] | *α, β*-pinene |
| 38.36 | 357.15509 | $C_{17}H_{26}O_8$ | Pinyl-diaterpenyl ester MW 358[11,12,13] | *α, β*-pinene |
| 40.15 | 367.17599 | $C_{19}H_{28}O_7$ | Pinonyl-pinyl ester MW 368[11,12,13] | *α, β*-pinene |
| 40.68 | 367.17599 | $C_{19}H_{28}O_7$ | Pinonyl-pinyl ester MW 368[11,12,13,14] | *α, β*-pinene |
| 41.58 | 387.20221 | $C_{19}H_{31}O_8$ | MW 388 dimer ester[11,12,13] | *α, β*-pinene |
| 45.53 | 337.20172 | $C_{19}H_{30}O_5$ | MW 337 dimer ester | unknown |
| 46.17 | 337.20172 | $C_{10}H_{18}O_5$ | MW 337 dimer ester | unknown |
| 42.76 | 369.19141 | $C_{19}H_{29}O_7$ | MW 369 dimer ester | unknown |

References: (1) Gómez-González et al. (2012); (2) Kourtchev et al. (2014); (3) Yasmeen et al. (2011); (4) Szmigielski et al. (2007); (5) Müller et al. (2012); (6) Putman et al. (2011); (7) Yu et al. (1999); (8) Glasius et al. (2000); (9) Carmedon et al. (2010); (10) Christoffersen et al. (1998); (11) Yasmeen et al. (2010); (12) Kristensen et al. (2013); (13) Kristensen et al. (2014); (14) Müller et al. (2008).

Table S2. P values derived from Analysis of Variances (ANOVA) test of variations in relative dimer to SOA concentrations at different ageing conditions.

| Ageing condition | *m/z* 357 | *m/z* 337 | *m/z* 343 | *m/z* 367 | *m/z* 387 | *m/z* 369 |
|---|---|---|---|---|---|---|
| dark ageing | 0.98 | 0.854 | 1 | 0.979 | 0.395 | 0.949 |
| UV&OH ageing | 0.829 | 0.333 | 0.533 | 0.533 | 0.8 | 0.933 |
| UV-only ageing | 0.933 | 0.933 | 0.933 | 0.933 | 0.533 | 0.933 |

$p \geq 0.05$ indicates no significant difference between the treatments. The relative dimer concentrations were obtained from the LC/MS analysis.

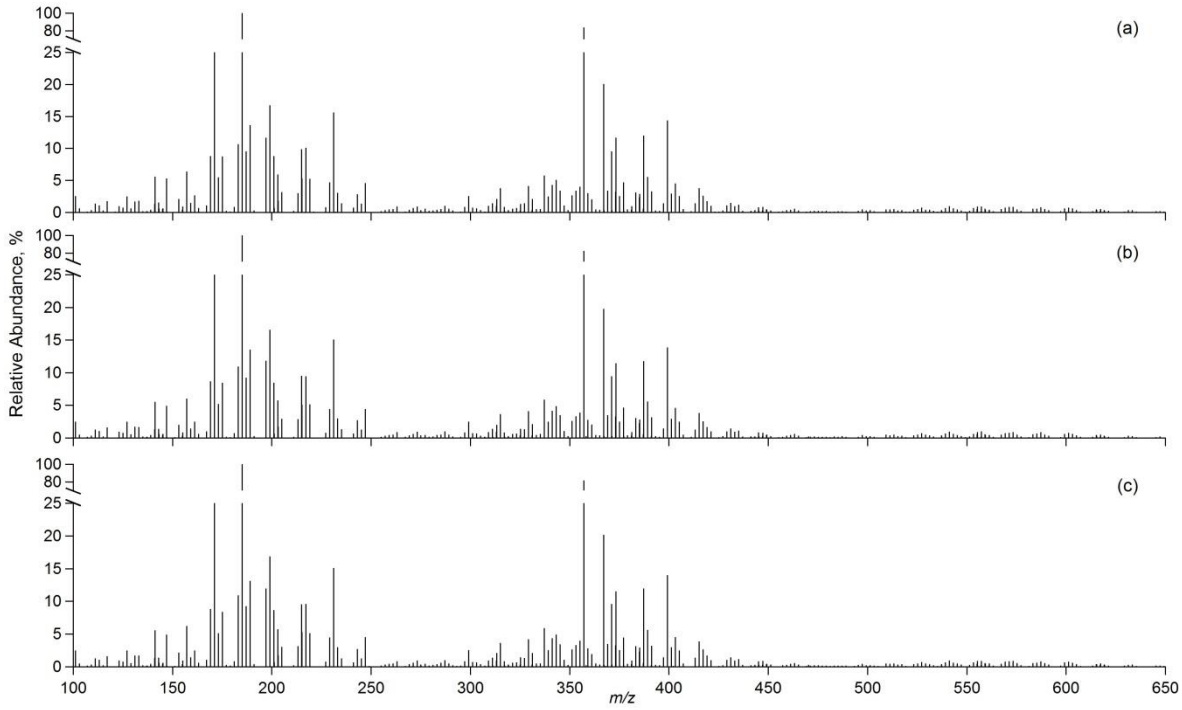


Fig. S1. Direct infusion (-) ESI-HR mass spectra of three analytical replicates (a) replicate 1 (b) replicate 2 and (c) replicate 3 of the 'fresh' SOA from dark ozonolysis of BVOC mixture.

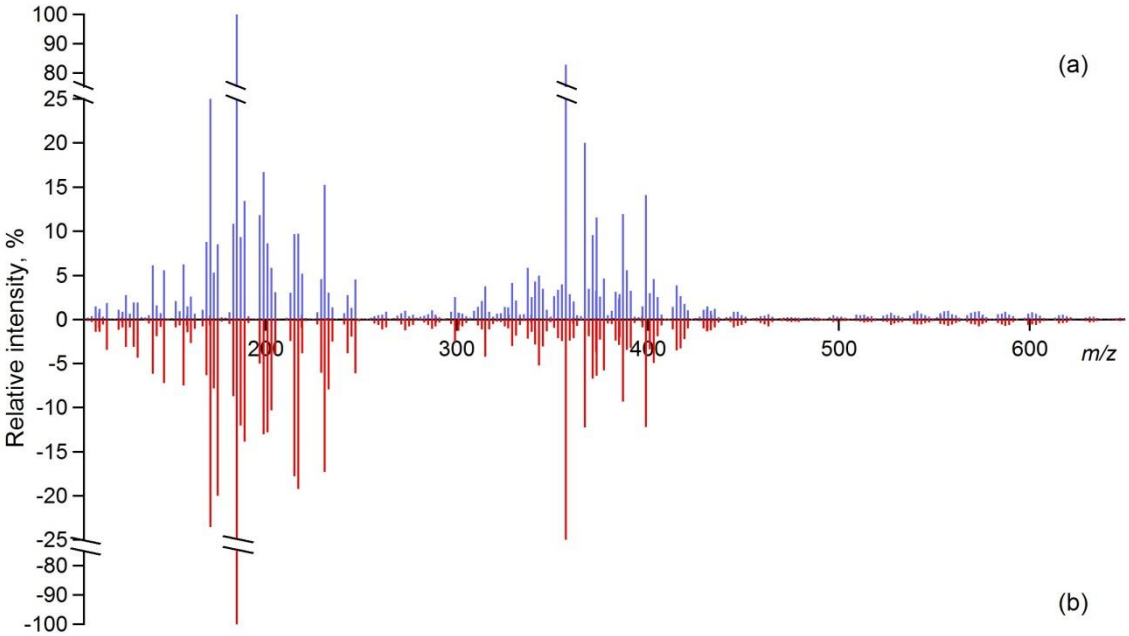


Fig. S2. Direct infusion (-) ESI-HR mass spectra showing 'common' ions for 'fresh' SOA from the dark ozonolysis of the BVOC mixture: (a) replicate 1 (b) replicate 2. The data for each smog chamber replicate was obtained from three analytical replicates. The data from one of the smog chamber replicates is inverted for clarity.

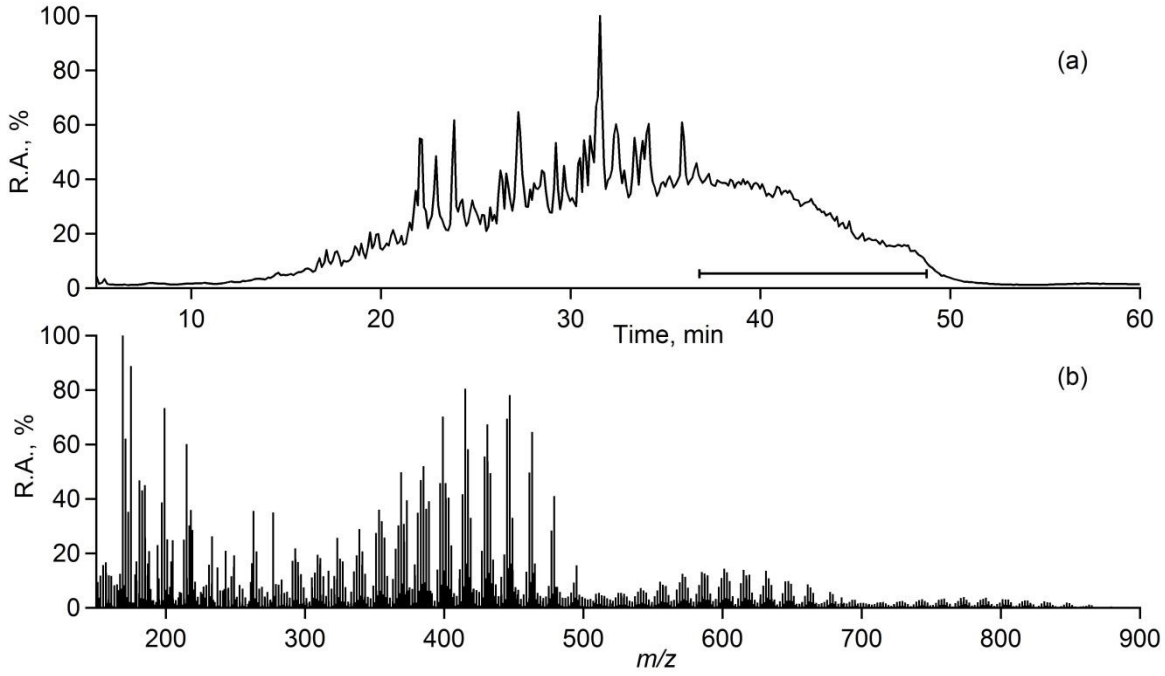


Fig. S3. (a) Total Ion Chromatogram of SOA from OH-initiated reaction with α-pinene; (b) (-) ESI-HR mass spectra showing high molecular weight compounds obtained by integration of chromatographic 'hump' between 36 and 48 min.

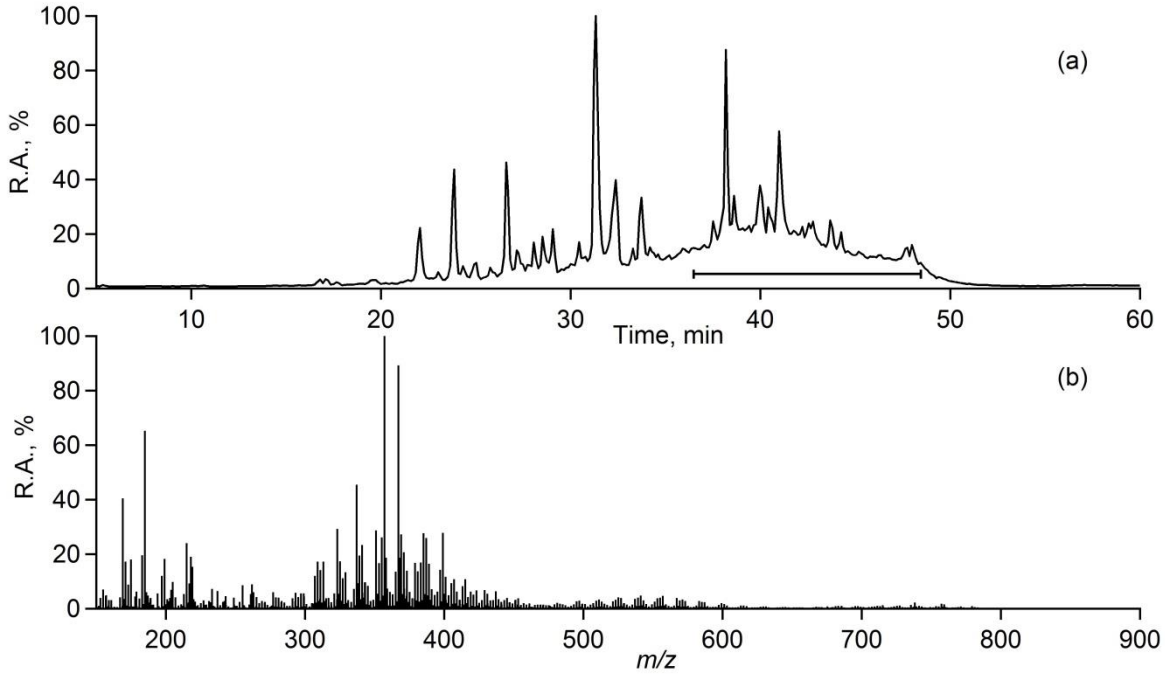


Fig. S4. (a) Total Ion Chromatogram of SOA from dark ozonolysis reaction with α-pinene in the presence of OH scavenger; (b) (-) ESI-HR mass spectra showing high molecular weight compounds obtained by integration of chromatographic 'hump' between 36 and 48 min. The resolved chromatographic peaks in (a) correspond to dimers with *m/z* 357; *m/z* 367 and *m/z* 387.

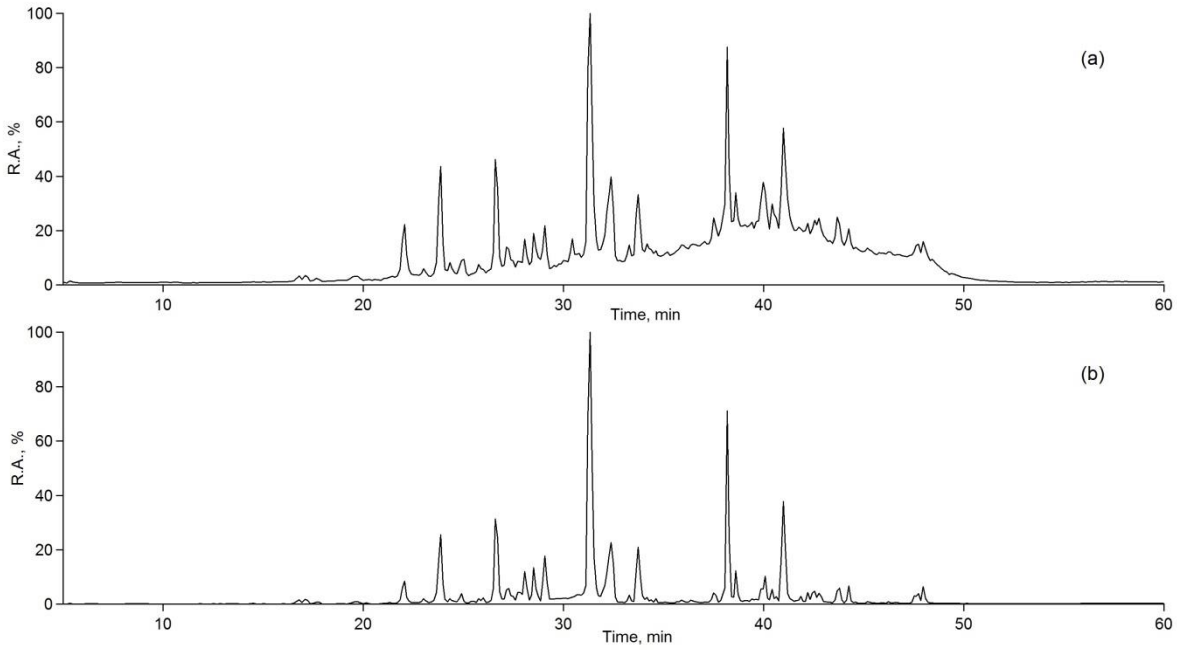


Fig. S5. (a) Total Ion Chromatogram (TIC) and (b) Base Peak (BP) chromatogram of SOA from OH-initiated reaction with α-pinene.

**References**

Camredon, M., Hamilton, J. F., Alam, M. S., Wyche, K. P., Carr, T., White, I. R., Monks, P. S., Rickard, A. R., and Bloss, W. J.: Distribution of gaseous and particulate organic composition during dark α-pinene ozonolysis, Atmos. Chem. Phys., 10, 2893–2917, 2010.

Christoffersen, T. S., Hjorth, J., Horie, O., Jensen, N. R., Kotzias, D., Molander, L. L., Neeb, P., Ruppert, L., Winterhalter, R., Virkkula, A., Wirtz, K., and Larsen, B. R.: cis-Pinic acid, a possible precursor for organic aerosol formation from ozonolysis of α-pinene, Atmos. Environ., 32, 1657–1661, 1998.

Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N. R., Hjorth, J., Kotzias, D., and Larsen, B. R.: Carboxylic acids in secondary aerosols from the oxidation of cyclic monoterpenes by ozone, Environ. Sci. Technol., 34, 1001–1010, 2000.

Gómez-González, Y., Wang, W., Vermeylen, R., Chi, X., Neirynck, J., Janssens, I. A., Maenhaut, W., and Claeys, M.: Chemical characterisation of atmospheric aerosols during a 2007 summer field campaign at Brasschaat, Belgium: sources and source processes of biogenic secondary organic aerosol, Atmos. Chem. Phys., 12, 125-138, 2012.

Kourtchev, I., Fuller, S. J., Giorio, C., Healy, R. M., Wilson, E., O'Connor, I., Wenger, J. C., McLeod, M., Aalto, J., Ruuskanen, T. M., Maenhaut, W., Jones, R., Venables, D. S., Sodeau, J. R., Kulmala, M., and Kalberer, M.: Molecular composition of biogenic secondary organic aerosols using ultrahigh-resolution mass spectrometry: comparing laboratory and field studies, Atmos. Chem. Phys., 14, 2155-2167, 2014.

Kristensen, K., Enggrob, K. L., King, S. M.,Worton, D. R., Platt, S. M., Mortensen, R., Rosenoern, T., Surratt, J. D., Bilde, M., Goldstein, A. H., and Glasius, M.: Formation and occurrence of dimer esters of pinene oxidation products in atmospheric aerosols, Atmos. Chem. Phys., 13, 3763–3776, 2013.

Kristensen, K., Cui, T., Zhang, H., Gold, A., Glasius, M., and Surratt, J. D.: Dimers in α-pinene secondary organic aerosol: effect of hydroxyl radical, ozone, relative humidity and aerosol acidity, Atmos. Chem. Phys., 14, 4201-4218, 2014.

Müller, L., Reinnig, M.-C., Warnke, J., and Hoffmann, Th.: Unambiguous identification of esters as oligomers in secondary organic aerosol formed from cyclohexene and cyclohexene/α- pinene ozonolysis, Atmos. Chem. Phys., 8, 1423–1433, 2008.

Müller, L., Reinnig, M. C., Naumann, K. H., Saathoff, H., Mentel, T. F., Donahue, N. M., and Hoffmann, T.: Formation of 3-methyl-1,2,3-butanetricarboxylic acid via gas phase oxidation of pinonic acid – a mass spectrometric study of SOA aging, Atmos. Chem. Phys., 12, 1483–1496, 2012.

Putman, A.L., Offenberg, J.H., Fisseha, R., Kundu, S., Rahn, T.A., and Mazzoleni, L.R., Ultrahigh-resolution FT-ICR mass spectrometry characterization of α-pinene ozonolysis SOA, Atmospheric Environment, 46, 164-172, 2012.

Szmigielski, R., Surratt, J. D., Gómez-González, Y., Van der Veken, P., Kourtchev, I., Vermeylen, R., Blockhuys, F., Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Edney, E. O., Seinfeld, J. H., Maenhaut, W., and Claeys, M.: 3-methyl-1,2,3- butanetricarboxylic acid: An atmospheric tracer for terpene secondary organic aerosol, Geophys. Res. Lett., 34, 6 pp., L24811, doi:10.1029/2007GL03133, 2007.

Yasmeen, F., Vermeylen, R., Szmigielski, R., Iinuma, Y., B¨oge, O., Herrmann, H., Maenhaut, W., and Claeys, M.: Terpenylic acid and related compounds: precursors for dimers in secondary organic aerosol from the ozonolysis of alpha- and beta-pinene, Atmos. Chem. Phys., 10, 9383–9392, 2010.

Yasmeen, F., Szmigielski, R., Vermeylen, R., Gómez-González, Y., Surratt, J. D., Chan, A. W. R., Seinfeld, J. H., Maenhaut, W., Claeys, M.: Mass spectrometric characterization of isomeric terpenoic acids from the oxidation of α-pinene, β-pinene, d-limonene, and Δ3-carene in fine forest aerosol. J. Mass Spectrom., 46, 425−442, 2011.

Yu, J., Cocker III, D. R., Griffin, R. J., Flagan, R. C., and Seinfeld, J. H.: Gas-phase ozone oxidation of monoterpenes: Gaseous and particulate products, J. Atmos. Chem., 34, 207–258, 1999.