1 # Acidic reaction products of mono- and sesquiterpenes in atmospheric fine particles in
2 a boreal forest
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4 Vestenius[1] M., Hellén[1] H., Levula[2] J., Kuronen[1] P., Helminen[3] K.J., Nieminen[2] T., Kulmala[2] M.
5 and Hakola[1] H.
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7 1) *Finnish Meteorological Institute, Atmospheric Composition Research, P.O. Box 503, 00101*
8 *Helsinki, Finland*
9 2) *Department of Physics, P.O. Box 64, FI-00014 University of Helsinki, Finland*
10 3) *Department of Chemistry, P.O. Box 55, FI-00014 University of Helsinki, Finland*
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12
13 Abstract
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15 Biogenic acids were measured in aerosols at the SMEAR II station (Station for Measuring Forest
16 Ecosystem-Atmosphere Relations II) in Finland from June 2010 until October 2011. The analysed
17 organic acids were pinic, pinonic, caric, limonic and caryophyllinic acids from oxidation of α-
18 pinene, β-pinene, limonene, Δ^3-carene and β-caryophyllene, respectively. Due to lack of authentic
19 standards, the caric, limonic and caryophyllinic acids were synthesized for this study. The mean,
20 median, maximum and minimum concentrations (ngm^{-3}) were as follows: limonic acid (1.26, 0.80,
21 16.5, below detection limit (<LOD)), pinic acid (5.53, 3.25, 31.4, 0.15), pinonic acid (9.87, 5.07,
22 80.1, <LOD), caric acid (5.52, 3.58, 49.8, <LOD) and caryophyllinic acid (7.87, 6.07, 86.1, <LOD).
23 The highest terpenoic acid concentrations were measured during the summer. Of the acids, β-
24 caryophyllinic acid showed the highest concentrations in summer, but during other times of the
25 year pinonic acid was the most abundant. The β-caryophyllinic acid contribution was higher than
26 expected, based on the emission calculations of the precursor compounds and yields from oxidation
27 experiments in smog chambers, implying that the β-caryophyllene emissions or β-caryophyllinic
28 acid yields were underestimated. The concentration ratios between terpenoic acids and their
29 precursors were clearly lower in summer than in winter, indicating stronger partitioning to the
30 aerosol phase during the cold winter season. The β-caryophyllinic and caric acids were weakly
31 correlated with the accumulation-mode particle number concentrations.
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33 **1. Introduction**
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35 Large amounts of biogenic volatile organic compounds (BVOCs) (isoprene, monoterpenes and
36 sesquiterpenes) are emitted to the atmosphere by vegetation, especially in the densely forested
37 boreal regions (Hakola et al., 2001, 2006; Tarvainen et al., 2005, 2007; Hellén et al., 2006;
38 Wiedinmyer et al., 2004; Steiner and Goldstein, 2007). In the atmosphere, these compounds are
39 oxidized, resulting in reaction products, e.g., acids and carbonyl-containing compounds that
40 participate in the formation and growth of new particles (Kulmala et al., 2004; Tunved et al., 2006).
41 Current estimates suggest that global biogenic secondary organic aerosol (SOA) sources are larger
42 than anthropogenic sources (Hallquist et al., 2009). Even though organic compounds account for
43 20-90% of the total fine particle mass concentration in a wide variety of atmospheric environments
44 (Kanakidou et al., 2005), little information is available on their detailed composition.
45
46 In smog chamber studies, the SOA yields for the various hydrocarbons and even for the
47 monoterpenes vary considerably (Griffin et al., 1999; Yu et al., 1999; Jaoui et al., 2003; Lee et al.,
48 2006). The produced compounds have very different vapour pressures, and partitioning between the

gas and aerosol phases varies widely. Therefore, detailed knowledge of the occurrence of individual compounds is essential for atmospheric studies.

Some studies have focused on the concentrations of the reaction products of α- and β-pinene (pinonic and pinic acids) in real atmospheres (Kavouras and Stephanou, 2002; Kourtchev et al., 2008, 2009; Zhang et al., 2010; Cheng et al., 2011; Kristensen and Glasius, 2011), but very little information is available on the concentrations of other terpenoic acids, mainly due to the lack of authentic standards. In some studies, the concentrations of other terpenoic acids were estimated by indirect calibration methods (Gomez-Gonzalez et al., 2012; Fu et al., 2009; Warnke et al., 2006). Sesquiterpene products are especially interesting, because their parent compounds are often too reactive to be measured in ambient air. β-Caryophyllene was the main sesquiterpene in many emission studies in boreal forests (Hakola et al., 2006; Tarvainen et al., 2005), but it has never been detected in the ambient air, due its high reactivity. β-Caryophyllene could be a major source of SOA, due to its reactivity and high aerosol yields in smog chamber studies (Jaoui et al., 2003; Lee et al., 2006; Chen et al., 2012).

In this study, specific acid reaction products of BVOCs, which affect the formation and growth of fine particles, were analysed from ambient aerosols in boreal forests. Fine particle filter samples were taken at the SMEAR II station (Station for Measuring Forest Ecosystem-Atmosphere Relations II; Hari and Kulmala, 2005) in Finland from June 2010 until October 2011.

2. Experimental

2.1 Sampling

The measurements were conducted at the SMEAR II station (61˚51'N, 24˚18'E, 181 m above sea level, a.s.l) at Hyytiälä, southern Finland (Hari and Kulmala, 2005). The largest nearby city is Tampere, with 200 000 inhabitants. It is located 60 km to the southwest of the site. The most common vegetation at the sampling site is a homogeneous Scots pine *Pinus sylvestris* L. forest, with some birches *Betula* and Norway spruces *Picea abies* growing nearby.

The aerosol samples were collected, using pumped sampling from June 2010 until October 2011, from the particulate matter (PM)$_{2.5}$ fractions in air onto quartz filters (Pallflex Tissuquartz 2500QAT-UP, internal diameter i.d. 47 mm; Pall Corp., Port Washington, NY, USA). A total of 86 samples were collected. Before sampling, the filters were heated to 600°C for over 8 h. Occasionally, we used an additional backup filter, but no breakthrough was observed. Airflow through the filters was 16 l min^{-1}. The collection times were 1-7 days per filter. The sampling dates are shown in Table 3. Longer, 7-day samples were collected during winter, due to expected low concentrations. Shorter, 1-3-day samples were collected during summer for better time resolution. Three-day samples were collected during the weekends. When calculating the monthly mean values, the samples were considered to belong to the month where most of the sampling took place. The gases were removed from the airflow before the filters, using a parallel-plate carbon denuder (Sunset Laboratory Inc., Portland, OR, USA). The efficiency of the denuder was checked by taking samples of VOCs (aromatic hydrocarbons and monoterpenes) more volatile than those measured in this study, using pumped adsorbent tube sampling and thermal desorpter-gas chromatography-mass spectrometry (TD-GC-MS) analysis. Aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylene), as well as monoterpene traces, were negligible after the denuder. The PM$_1$ concentrations were measured, using Dekati model PM10 impactors (Dekati, Tampere, Finland) at the same site and time period as the terpenoic acids.

2.2 Sample preparation and analysis

The samples were extracted into 50 ml of methanol (J.T.Baker 8402; Mallinkrodt Baker, now Avantor Performance Materials Inc., Center Valley, PA, USA), using an ultrasonic bath for 90 min and then evaporated into a 1-ml volume, using a Büchi Syncore evaporator (Büchi Labortechnik AG, Flawil, Switzerland), and further evaporated into 100 µl under nitrogen flow. The samples were analysed using high-performance liquid chromatography with electrospray ionization and an ion trap mass spectrometer (HPLC-ESI-ITMS) (Agilent 1100 Series LC/MSD Trap; Agilent Technologies, Santa Clara, CA, USA) in negative-ion mode. The column used was a Waters XTerra ® MS C_{18} (3.5 µm, 2.1 x 150 mm) (Waters Corp., Milford, MA, USA). The main components of the mobile phase were MilliQ water (Millipore Corp., Billerica, MA, USA) and acetonitrile (ACN) (VWR HiPerSolv Chromanorm; VWR International, Radnor, PA, USA). The pH of the mobile phase was adjusted to ~3 with acetic acid (Fluka 99.5 %). The 80-min-long gradient program was initiated with 95% water and 5% ACN, and after 5 min the ACN was gradually increased to 8% at 10 min. After 10 min, the ACN concentration was held at 8% until 40 min, and thereafter quickly increased to 90% at 45 min and to 95% at 50 min. The concentration was then held constant until 70 min and later decreased to 5% at 71 min and held at 5% until the end of the run. The column was held at a constant temperature of 65 ˚C. The samples were analysed using external standards on a four-point calibration curve representing the entire measurement area. The uncertainty of the analysis based on duplicate analysis was less than 50% close to the detection limits, and less than 20% for higher concentrations. Camphoric acid was used as an internal standard to correct for losses in sample preparation, matrix effects and changes in sensitivity of the instrument. The concentrations of the analytes in the samples varied between below detection limit and 145 ng m^{-3}. The limit of detection was calculated using the standard deviation of the blank samples, and was typically from 0.1 to 0.8 ng m^{-3}, being lowest for the limonic acid. The variation was lower within compounds than between compounds. Each of the compounds was measured individually, using the mass spectrometer's scan mode to determine the retention times and representative ions for each compound from the standard solution. In the analysis runs, the detector was used in multiple reaction monitoring (MRM) mode, in which each compound was monitored in its own retention time window, using its representative ion.

2.3 Synthesis of *cis*-3-caric, limonic and β-caryophyllinic acids

We selected the main acid products (e.g. Yu et al., 1999; Jaoui et al., 2006) of the most common monoterpenes (α-pinene, β-pinene, 3-carene, limonene) and the most common sesquiterpene, i.e. β-caryophyllene, emitted in boreal forests (Tarvainen et al., 2007) as target compounds of the study. The pinic and pinonic acids were commercially available, but the β-caryophyllinic acid, *cis*-3-caric acid and limonic acid (Fig. 1) were synthesized at the Laboratory of Organic Chemistry, University of Helsinki.

The nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity Inova 500 spectrometer (Varian Medical Systems, Palo Alto, CA, USA). The mass spectra were obtained with a Bruker microTOF (ESI-time-of-flight, ESI-TOF) (Bruker Corp., Billerica, MA, USA) or JEOL JMS-700 (electron ionization-MS, EI-MS) (JEOL Ltd., Tokyo, Japan) instruments. The infrared (IR) spectra were recorded on a Bruker Alpha-P Fourier-transform-IR (FT-IR) instrument. The melting points (Mp) were determined in open capillary tubes with a Büchi B-545 apparatus.

Cis-3-caric acid was prepared from *delta*-3-carene (Aldrich, 95% purity; Sigma-Aldrich, St. Louis, MO, USA) by $RuCl_3$-catalysed oxidation with $NaIO_4$ (Aldrich) to *cis*-3-caronic acid (Nair et al., 2010) and subsequent haloform reaction with NaOBr in aqueous NaOH (Semmler and von Schiller, 1927) to the final product. The product was purified by recrystallization from cyclohexane-toluene-

149 isopropanol to give a white powder with 10% overall yield and 95% purity (estimated by NMR).
150 Mp. 109-112 °C (lit. 112-113 °C, Semmler and von Schiller, 1927). ^{1}H NMR (CDCl$_3$, 500 MHz) δ:
151 12.22 (br, 2H, 1 & 6 COOH), 2.62 (dd, J = 17 Hz, 3.5 Hz, 2H, 2 & 5), 2.03 (m, 2H, 2 & 5), 1.04 (s,
152 3H, 8), 1.01 (m, 2H, 3 & 4), 0.92 (s, 3H, 9); ^{13}C NMR (CDCl$_3$, 126 MHz) δ: 180.9 (1 & 6), 30.2 (2
153 & 5), 28.5 (8), 22.0 (3 & 4), 17.3 (7), 15.4 (9). High-resolution MS (HRMS) (ESI-TOF) mass-to-
154 charge ratio (m/z) calculated for C$_9$H$_{14}$NaO$_4$ (M+Na) 209.0784, found 209.0788. IR attenuated total
155 reflection (ATR) ν: 3013 cm^{-1}, 2992 cm^{-1}, 2919 cm^{-1}, 2868 cm^{-1}, 2849 cm^{-1}, 2655 cm^{-1}, 2620 cm^{-1},
156 2591 cm^{-1}, 2551 cm^{-1}, 1694 cm^{-1}, 941 cm^{-1}, 923 cm^{-1}, 905 cm^{-1}.

157 Limonic acid was prepared, starting from (R)-limonene (Aldrich, 97% purity), which was
158 epoxidized with *meta*-chloroperbenzoic acid (Aldrich, 85%) and NaHCO$_3$ in dichloromethane
159 (DCM) to limonene epoxide (Naves and Grampoloff, 1961). Oxidative ring opening of the epoxide
160 with NaIO$_4$ (Aldrich, 99.8%) in water-tetrahydrofuran (THF) (Cane et al., 1992) resulted in
161 limonon aldehyde, which was oxidized with NaClO$_2$ (Aldrich, 80%) in dimethyl sulphoxide
162 (DMSO) (Binder et al., 2008) to limononic acid. The ketoacid was esterified with ethyl bromide
163 and NaHCO$_3$ in DMSO (Bocchi et al., 1979) and purified by flash chromatography (solvent
164 gradient from pentane to 1:1 Et$_2$O-pentane) to give ethyl limononate as a colourless oil. Thin-layer
165 chromatography (TLC) r$_F$: 0.37 (EtOAc:hexane 1:2, vanillin staining). ^{1}H NMR (CDCl$_3$, 500 MHz)
166 δ: 4.77 (d, J = 28 Hz, 2H, 10), 4.10 (q, J = 7.2 Hz, 2H, 11), 2.55 (m, 1H, 5), 2.40-2.31 (m, 4H, 3 &
167 6), 2.12 (s, 3H, 1), 1.74-1.67 (m, 1H, 4), 1.64 (s, 3H, 8), 1.64-1.58 (m, 1H, 4), 1.23 (t, J = 7.2 Hz,
168 3H, 12); ^{13}C NMR (CDCl3, 126 MHz) δ: 208.5 (s, 2), 172.4 (7), 145.5 (9), 113.0 (10), 60.4 (11),
169 43.3 (5), 41.3 (3), 39.3 (6), 30.1 (1), 26.4 (4), 18.5 (8), 14.3 (12). HRMS (ESI-TOF) m/z calculated
170 for C$_{12}$H$_{20}$NaO$_3$ (M+Na) 235.1305, found 235.1313. IR (ATR) ν: 3075 cm^{-1}, 2982 cm^{-1}, 2937 cm^{-1},
171 1731 cm^{-1}, 1715 cm^{-1}, 1646 cm^{-1}, 894 cm^{-1}.

172 Haloform reaction of ethyl limononate with NaOBr in dioxane/water (Staunton and Eisenbraun,
173 1973) yielded limonic acid, which was purified by flash chromatography on silica (solvent gradient
174 from 50:1 CHCl$_3$-AcOH to 5:45:1 MeOH-CHCl$_3$-AcOH) to give a white solid with 24% yield
175 (based on limonene) and 97% purity (estimated by NMR). Mp. 115-117 °C (lit. 117-118 °C; Abe,
176 1943). [α]$_D$^{22,6} = +7.416 (c = 0.5, *i*-PrOH). ^{1}H NMR (acetone-d6, 500 MHz) δ: 10.48 (br, 2H, 1 & 6
177 COOH), 4.80 (d, J = 12 Hz 2H, 9), 2.62 (m, 1H, 4), 2.44-2.36 (m, 2H, 5), 2.31-2.20 (m, 2H, 2),
178 1.83-1.76 (m, 1H, 3), 1.73-1.65 (m, 1H, 3), 1.70 (s, 3H, 7); ^{13}C NMR (acetone-d6, 126 MHz) δ:
179 174.5 (1), 173.4 (6), 147.0 (8), 112.8 (9), 43.8 (4), 39.2 (5), 32.0 (2), 28.6 (3), 19.0 (7). HRMS
180 (ESI-TOF) m/z calculated for C$_9$H$_{14}$NaO$_4$ (M+Na) 209.0784, found 209.0780. IR (ATR) ν: 3081
181 cm^{-1}, 2976 cm^{-1}, 2941 cm^{-1}, 2911 cm^{-1}, 2668 cm^{-1}, 2573 cm^{-1}, 1699 cm^{-1}, 1694 cm^{-1}, 1647 cm^{-1}, 896
182 cm^{-1}.

183 β-Caryophyllinic acid was prepared from β-caryophyllene oxide (Aldrich, 99% purity) by a method
184 that will be published separately. It was obtained as a glassy solid of > 98% purity after flash
185 chromatography on silica (solvent gradient from 50:1 CHCl$_3$-AcOH to 5:45:1 MeOH-CHCl$_3$-
186 AcOH). TLC r$_F$ 0.62 (10:90:2 MeOH-DCM-AcOH, Ce-phosphomolybdate staining). ^{1}H NMR
187 (CDCl$_3$, 500 MHz) δ: 10.89 (br, 4 & 5 COOH), 4.76 (s, 1H, 14), 4.72 (s, 1H, 14), 2.50 (t, J = 7.7
188 Hz, 2H, 6), 2.42 (q, J = 9.3 Hz, 1H, 9), 2.35-2.22 (m, 4H, 3 & 7), 1.94 (dt, J = 9.2, 7.7 Hz, 1H, 1),
189 1.81 (dd, J = 8.3 Hz, 10.2 Hz, 1H, 10), 1.71 (q, J = 7.7 Hz, 2H, 2), 1.47 (t, J = 10.2 Hz, 1H, 10),
190 1.06 (s, 3H, 12), 1.06 (s, 3H, 13); ^{13}C NMR (CDCl$_3$, 126 MHz) δ: 180.2 (4), 179.8 (5), 150.5 (8),
191 107.8 (14), 47.9 (1), 41.8 (9), 39.6 (10), 33.8 (11), 32.6 (6), 32.6 (3), 31.1 (12), 28.9 (7), 25.7 (2),
192 22.4 (13). HRMS (EI), derivatization with N,O-*bis*(trimethylsilyl)trifluoroacetamide (BSTFA) to
193 *bis*-trimethylsilyl ester, m/z calculated for C$_{20}$H$_{38}$O$_4$Si$_2$ (M$^+$) 398.2327, found 398.2318. EI-MS (70
194 eV) m/z (%): 400 (3), 399 (4), 398 (12) [M], 385 (6), 384 (13), 383 (50) [M-CH$_3$], 355 (8) [M-
195 CH$_3$-CO], 328 (7) [M-C$_5$H$_{10}$], 313 (26), 309 (100), 299 (37), 279 (19), 200 (81) [M-2(C$_5$H$_{10}$)], 149
196 (67) 117 (85).

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3. Results and discussion

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3.1 Annual variability of terpenoic acids

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The highest terpenoic acid concentrations were measured during summer (Fig. 2), but high concentrations were measured occasionally also during winter, especially of pinonic acid. Hakola et al. (2012) measured BVOC concentrations at the same site and found occasionally very high BVOC concentrations originating from the nearby sawmills. These emissions cause high concentrations of aerosol particles (Liao et al., 2011) and may cause high acid concentrations as well. At least reactions with nitrate radicals are fast enough to produce acids in less than half an hour (Hakola et al., 2003). The results are tabulated in Table 3, which also shows the length of each measurement. Table 1 shows the seasonal average concentrations. Those values below the detection limit were taken as half of the detection limits in calculation of averages. β-Caryophyllinic acid showed the highest concentrations in summer, but during other times of the year pinonic acid was the most abundant. β-Caryophyllene is emitted mainly in July (Hakola et al., 2006), so the product concentrations are expected to peak at that time too. Limonic acid emissions are distributed more evenly throughout the year, with a maximum already in spring. Scots pine emits only small amounts of limonene, but Norway spruce emits limonene mainly in May (Hakola et al., 2003). There are also few birches growing in the area and birches emit limonene early summer (Hakola et al., 2001). The concentrations were also studied in relation to meteorological parameters, such as temperature, wind speed, relative humidity and the amount of rain at sampling time, but no clear correlations were found. Averaging over the whole day or several days complicates this inspection.

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The acid concentrations were higher in 2011 than in 2010. The temperatures at the time of the measurements were several degrees lower in 2011 than in 2010 (the difference was 2.7°C in July and 4.3°C in August) and colder temperatures could have caused higher concentrations in the aerosol phase, although the emissions were probably higher at warmer temperatures. Kamens and Jaoui (2001) showed in their simulations and smog chamber experiments with α-pinene that decreasing the temperature by 10 °C increased aerosol yields by a factor of ~2.

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The concentrations of pinonic and pinic acids had relatively good correlation during the summer months ($r^2 = 0.42$). This was expected, since they have the same precursors, i.e. they are both reaction products of α- and β-pinene. The average concentrations for pinonic acid were 40% higher than for pinic acid. Caric acid and caryophyllinic acid were also somewhat correlated ($r^2 = 0.47$) in summer.

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The pinic and pinonic acids were also measured previously at the SMEAR II station in short 1- or 2-month campaigns in spring and summer. The results from these previous studies are listed in Table 2. Kourtchev et al. (2008) measured pinic acid in July-August 2005 in the PM_1 fraction and found a median value of 7.7 ng m^{-3}, which is similar to the summer median in our measurements (6.7 ng m^{-3}). Other results (Warnke et al. 2006, Kourtchev et al., 2008, Parshintsev et al. 2010) also showed values similar to ours.

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3.2 Comparison of terpenoic acids with corresponding monoterpenes

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Ambient monoterpene concentrations were measured at the same site from October 2010 until November 2011 near the filter-sampling site by in-situ TD-GC-MS. Detailed description of the monoterpene measurements can be found in Hakola et al. (2012). In Figure 2, we compared the

248 BVOC mixing ratios with the corresponding acid concentrations and found that the overall seasonal
249 patterns were similar, although not all the acid peaks were seen in the parent monoterpene data.
250 This was expected, since the measurement times of the VOCs and corresponding acids did not
251 cover whole months and did not always match. In the on-line VOC measurements, there were
252 several breaks due to malfunction of the instrument and because the sampling times of the acids
253 where sometimes several days, the overlapping of VOC and acid data are not complete. Thus
254 comparing these seasonal means represents approximates only. However, since the daily variation
255 in VOC mixing ratios is quite modest compared to the seasonal variability, it is justified to compare
256 VOC and acid concentrations. The seasonal means of the acid and monoterpene concentrations and
257 the ratios between the acids and precursor monoterpenes are tabulated in Table 1.

259 We calculated the seasonal acid/monoterpene ratios and they were lower in summer than in winter
260 (Table 1). This could indicate that during cold seasons the acids are partitioned more to the particle
261 phase than to the gas phase and vice versa during warm seasons. Temperature, together with carbon
262 and oxygen numbers, are known to be controlling factors in phase partitioning of organic acids
263 (Finlayson-Pitts and Pitts, 2000).

265 Tarvainen et al. (2007) calculated the BVOC emissions in the Middle Boreal Zone in Finland,
266 utilizing satellite land-cover information, actual meteorological data and published emission factors
267 in a Biogenic Emissions Inventory System (BEIS)-type canopy emission model. They did not
268 calculate the emissions for β-caryophyllene, but rather for total sesquiterpenes. However, in the
269 published sesquiterpene emission rates (Hakola et al., 2006; Tarvainen et al., 2005), β-
270 caryophyllene was clearly the predominant sesquiterpene species emitted in boreal forests. We
271 compared these emissions with the corresponding acid concentrations (Fig. 3) and found that they
272 were in relatively good agreement. The pinic and pinonic acids and α- and β-pinenes are added
273 together since both of these monoterpenes produce both acids. The caric and limonic acids showed
274 lower contributions than their precursors in the emission calculations. This was expected, since their
275 yields in the smog chamber experiments were lower than the yields of the other acids (Yu et al.,
276 1999; Jaoui et al., 2006, 2003). However, the yield of β-caryophyllinic acid (Jaoui et al., 2003) was
277 also lower than the pinic and pinonic acid yields, but its contribution was higher than expected,
278 based on the emission calculations, especially since the calculations also included other
279 sesquiterpenes. This could imply that the β-caryophyllene emissions or β-caryophyllinic acid yields
280 were underestimated.

282 **3.3 Comparison with particulate data**

284 The highest seasonal means for PM_1 were observed in summer, together with the highest terpenoic
285 acid concentrations (Table 1), but the measured terpenoic acids explained only small fraction of
286 total PM_1 mass, 0.2% in winter and 0.7% in summer.

288 The average submicrometre organic carbon (OC) concentration in Hyytiälä in 2007/2008 was 1100
289 ng m^{-3}, 1200 ng m^{-3} in summer and 1300 ng m^{-3} in winter (Aurela et al., 2011). The sum of the
290 terpenoic acids measured in this study comprised only 0.9-3.4% of this OC, showing the highest
291 fraction in summer and lowest in winter. Although the measurements were conducted in different
292 years, we expected that these five terpenoic acids would have only a small impact on the total OC
293 concentrations, especially in winter. However, this fraction was clearly higher than the 0.6% value
294 for the 12 terpenoic acids found by Gomez-Gonzalez et al. (2012) in summer in a forest site in
295 Belgium.

The acid concentrations were also studied in relation to the particle concentrations in different size fractions. The particle number concentrations were measured in the size range 3-1000 nm with a differential mobility particle sizer (DMPS) and the PM_1 mass concentration was calculated from it (Aalto et al., 2001). No correlation was found between the acid concentrations and the nucleation-mode particles (3-25 nm) or the Aitken-mode particles (25-100 nm). In the accumulation-mode particles (100-1000 nm), the caric (r^2=0.28) and caryophyllinic (r^2=0.13) acids were somewhat correlated with the particle number concentration, as shown in Fig. 4. The PM_1 mass concentration correlated weakly with the caric (r^2=0.28) and caryophyllinic (r^2=0.1) acids. The pinic and pinonic acids did not correlate with any particle-size fractions. Smog chamber studies showed that pinonic and pinic acids are partitioned more to the gas phase than the other studied acids (Yu et al., 1999).

4. Conclusions

The highest terpenoic acid concentrations were measured in summer. The results were compared with the parent mono- and sesquiterpene mixing ratios. Pinonic and β-caryophyllinic acids were the most abundant acids in summer. The β-caryophyllinic acid contribution was higher than expected, based on the emission calculations and smog chamber yields, implying that the β-caryophyllene emissions and/or β-caryophyllinic acid yields were underestimated. The limonic acid concentration peaked already in spring, which is in accordance with the measured limonene emissions from Norway spruce, which also reach their maximum in spring. The pinonic and limonic acids also showed quite high concentrations in winter. These winter concentrations may be of anthropogenic origin. Higher ratios between the terpenoic acids and their precursors in winter indicated higher partitioning to the aerosol phase during the colder winter months.

These five terpenoic acids comprised only a small fraction (~1-3%) of the total OC in particles measured at the site and only 0.2-0.7% of the PM_1 mass. The β-caryophyllinic and caric acids were weakly correlated with the accumulation-mode particle number concentrations, implying that they participated in the particle growth process, which is crucial for formation of cloud condensation nuclei.

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Table 1. Seasonal mean concentrations (standard deviations) of terpenoic acids from this study and precursor monoterpenes from Hakola et al. (2012) in Hyytiälä (June 2010-October 2011). Also included are the ratios between acids and precursors (%) and mean PM_1 concentrations.

|	winter	spring	summer	autumn
Terpenoic acids (ng m^{-3})				
Limonic acid	0.6 (0.5)	1.7 (0.9)	1.4 (2.4)	1.1 (0.9)
Pinic acid	1.7 (1.4)	2.6 (3.2)	7.2 (7.3)	3.6 (4.8)
Pinonic acid	10.2 (18)	6.5 (3.3)	10.7 (13.6)	8.3 (9.6)
Caric acid	2.6 (1.4)	3.6 (0.9)	7.2 (8.6)	2.9 (2.6)
Caryophyllinic acid	1.2 (0.8)	4.5 (4.2)	10.9 (12.1)	3.8 (5.0)
Monoterpenes (ng m^{-3})				
α-pinene	40 (230)	180 (530)	1070 (1030)	220 (220)
β-pinene	4 (30)	20 (30)	300 (310)	40 (40)
α-pinene+β-pinene	40	200	1370	260
Δ^3-carene	20 (100)	60 (230)	480 (520)	110 (110)
Limonene	10 (40)	10 (40)	130 (150)	20 (20)
Ratios (%)				
Pinic acid/(α-pinene+β-pinene)	4.3	1.3	0.5	1.4
Pinonic acid/(α-pinene+β-pinene)	11	3.3	0.8	3.2
Limonic acid/limonene	5.5	17	1.1	4.9
Caric acid/Δ3-carene	12	5.7	1.5	2.6
PM_1 (µg m^{-3})	4.8	3.1	5.3	2.9

Table 2. Concentrations of pinic and pinonic acids in comparison to previous studies at the SMEAR II station in Hyytiälä

ng m^{-3}	Pinic acid	Pinonic acid	PM size cutoff	Reference
Spring				
Mar/Apr -03	1.1-21	0.99-74	PM2.5	Warnke et al. 2006
Mar/Apr -11	0.66-7.3	0.5-11	PM2.5	This study
Summer				
Jul/Aug -01	0.38-4.7	0.91-8.2	PM2.5	Warnke et al. 2006
Jul/Aug -05	2-29.6		PM1	Kourtchev et al., 2008
Aug -07	1-7	11-28	PM2.5	Parshintsev et al. 2010
Jul/Aug -10/11	0.64-31	0.1-80	PM2.5	This study

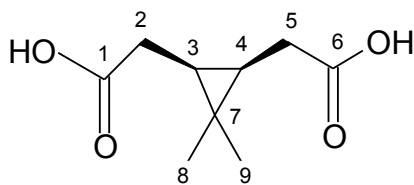a)
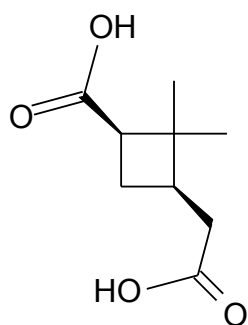
Pinic acid
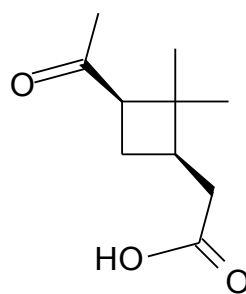
cis-Pinonic acid

b)

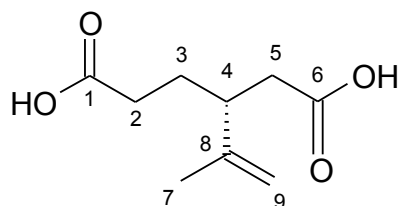*Cis*-3-caric acid   Limonic acid   β−Caryophyllinic acid
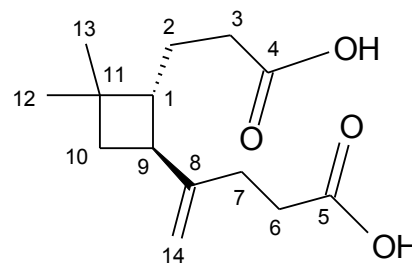
Figure 1. Structures of a) commercially available and b) synthesized terpenoic acids.
The numbers refer to the C atoms in the NMR spectra.
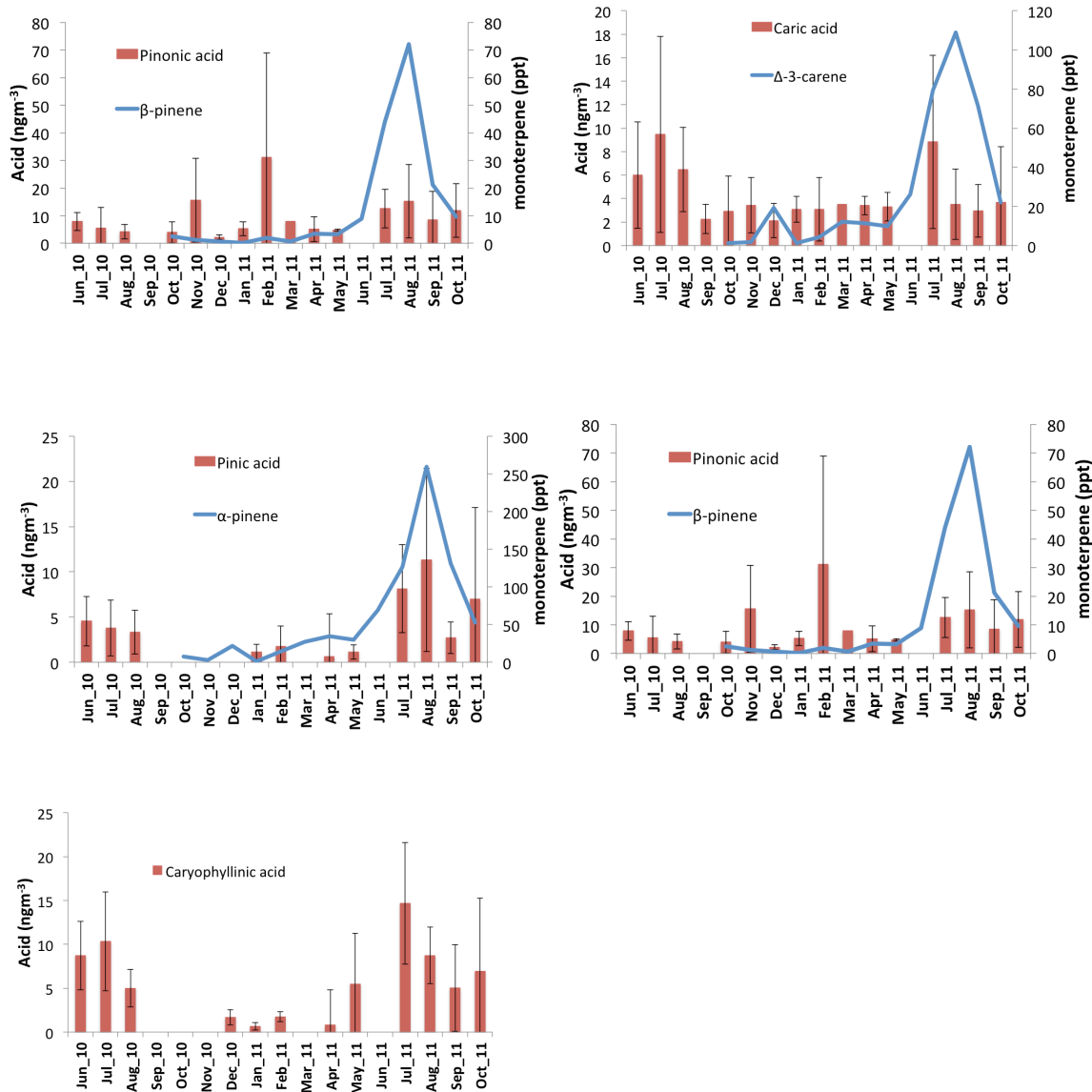
Figure 2. Monthly mean terpenoic acid concentrations and their standard deviations together with monthly mean monoterpene concentrations from Hakola et al. (2012).

Figure 3. Relative contributions of terpenoic acids in summer (left) and average terpenoid emission fluxes (right) from Middle Boreal Zone forests in summer from Tarvainen et al. (2007).

4a)

4b)

Figure 4. Correlations between caric acid (4a) and β-caryophyllinic acid (4b) and the accumulation-mode particle number concentrations.

Table 3. Sampling dates and acid concentrations of all samples.

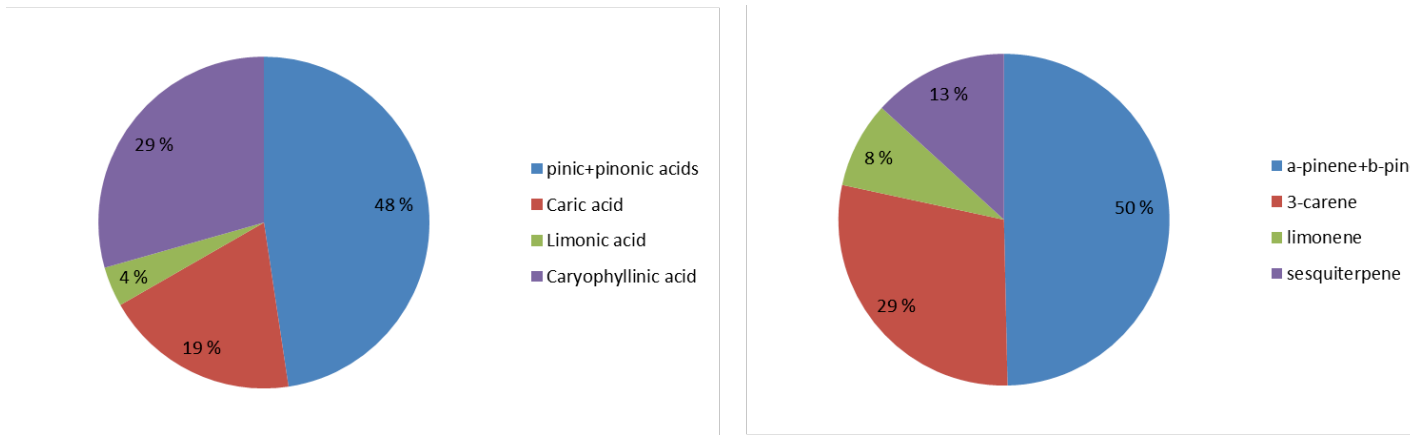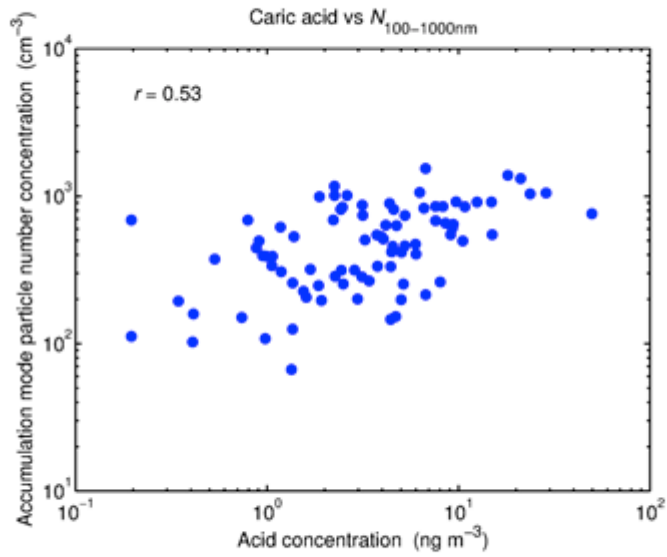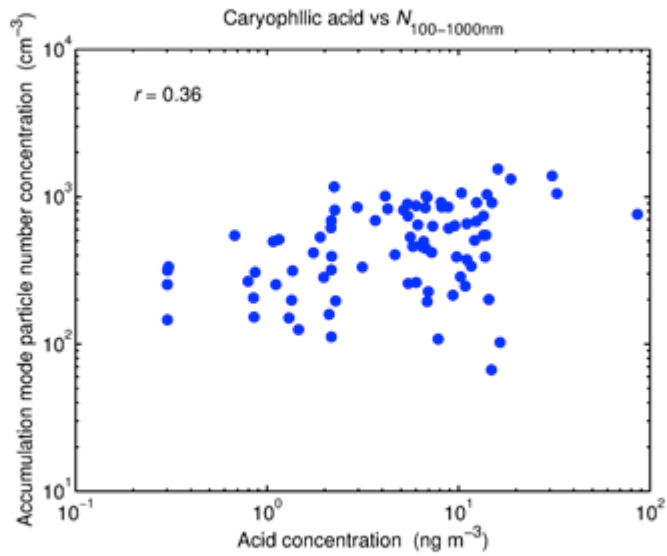| START	END	Limonic acid ng m^{-3}	Pinic acid ng m^{-3}	Pinonic acid ng m^{-3}	Caric acid ng m^{-3}	Caryophyllinic acid ng m^{-3}
100604	100607	0.71	4.86	8.10	2.27	10.25
100607	100609	1.10	<LOD	7.18	5.96	6.40
100609	100611	1.62	0.52	11.35	14.87	12.44
100611	100614	0.35	2.64	13.68	1.07	13.79
100614	100616	2.45	7.28	6.77	9.10	13.50
100616	100618	1.98	<LOD	3.12	4.42	<LOD
100621	100623	0.33	7.29	8.91	1.36	5.47
100628	100630	1.41	4.94	4.01	5.25	5.45
100630	100702	3.24	7.28	8.02	9.72	8.10
100705	100707	<LOD	<LOD	<LOD	21.13	18.77
100707	100709	<LOD	<LOD	<LOD	23.69	14.09
100709	100712	<LOD	<LOD	<LOD	<LOD	<LOD
100716	100719	<LOD	<LOD	<LOD	4.37	5.41
100719	100721	<LOD	<LOD	<LOD	2.43	<LOD
100723	100726	2.08	5.77	2.46	9.30	8.89
100726	100728	1.29	2.34	8.50	6.27	10.36
100729	100730	1.46	8.53	23.21	6.73	16.05
100730	100802	0.72	1.78	2.22	2.22	3.67
100802	100804	1.97	7.28	7.35	9.39	6.13
100804	100806	0.88	3.49	5.74	7.59	8.82
100806	100809	0.74	4.86	2.07	2.25	4.14
100811	100813	<LOD	<LOD	6.72	10.80	2.96
100813	100816	<LOD	<LOD	<LOD	6.59	4.27
100915	100922	2.39	<LOD	<LOD	3.13	<LOD
100922	100930	<LOD	<LOD	<LOD	1.38	<LOD
101004	101011	<LOD	<LOD	<LOD	<LOD	<LOD
101025	101101	<LOD	<LOD	6.68	5.03	<LOD
101108	101119	1.98	<LOD	32.99	5.16	<LOD
101119	101122	<LOD	<LOD	8.27	4.43	<LOD
101122	101129	0.15	0.15	5.50	0.74	1.30
101129	101207	<LOD	<LOD	2.55	3.74	0.68
101213	101220	<LOD	<LOD	<LOD	1.68	<LOD

101227	110103	<LOD	<LOD	<LOD	<LOD	<LOD
110103	110110	1.47	2.12	8.65	4.05	1.15
110110	110117	<LOD	<LOD	4.33	2.86	<LOD
110118	110125	<LOD	<LOD	2.78	3.77	<LOD
110125	110201	0.50	<LOD	5.20	1.60	<LOD
110201	110207	0.53	0.17	4.24	5.01	1.34
110214	110221	<LOD	<LOD	57.87	1.17	<LOD
110228	110307	<LOD	<LOD	4.40	2.50	<LOD
110328	110404	1.04	7.28	11.39	4.53	6.47
110426	110502	0.78	<LOD	5.09	3.41	0.79
110502	110509	2.42	<LOD	4.45	2.44	1.36
110516	110524	2.48	1.70	5.06	4.16	9.56
110630	110701	3.71	29.37	35.21	18.10	30.84
110701	110704	16.46	16.06	80.14	49.78	86.09
110704	110705	0.55	21.85	23.03	0.98	7.83
110705	110706	1.83	<LOD	23.02	4.47	7.25
110706	110706	<LOD	0.00	<LOD	14.99	<LOD
110711	110712	5.75	9.17	9.94	28.66	32.68
110712	110713	<LOD	10.98	<LOD	0.91	<LOD
110713	110714	<LOD	14.48	<LOD	<LOD	<LOD
110714	110715	<LOD	<LOD	<LOD	1.55	<LOD
110715	110718	1.21	<LOD	<LOD	4.74	7.33
110718	110719	<LOD	<LOD	<LOD	3.14	<LOD
110719	110720	1.05	<LOD	20.64	7.59	12.38
110720	110721	1.24	<LOD	7.38	12.49	14.96
110721	110722	<LOD	<LOD	<LOD	8.29	8.17
110725	110726	0.87	<LOD	11.08	2.47	6.70
110726	110727	<LOD	5.35	<LOD	2.61	<LOD
110728	110729	1.02	16.55	12.85	3.16	13.50
110729	110801	0.89	<LOD	4.59	3.96	5.61
110801	110802	<LOD	20.71	12.70	1.86	10.84
110802	110803	1.82	13.81	19.38	0.53	11.06
110804	110805	<LOD	<LOD	22.65	8.56	11.05
110805	110808	0.81	<LOD	<LOD	4.59	5.17
110808	110809	0.94	15.22	5.88	0.99	9.78
110809	110810	1.33	20.56	28.95	1.06	11.65
110811	110812	<LOD	<LOD	<LOD	6.74	9.34
110815	110816	3.37	31.40	43.34	3.25	12.15

110816	110817	2.27	<LOD	20.11	8.03	6.02
110818	110819	<LOD	<LOD	10.30	0.88	<LOD
110826	110829	0.30	<LOD	<LOD	2.25	<LOD
110901	110907	2.81	4.03	3.35	5.23	5.78
110909	110912	2.11	<LOD	9.65	6.00	4.66
110916	110919	<LOD	<LOD	<LOD	1.92	<LOD
110919	110921	<LOD	<LOD	<LOD	1.18	<LOD
100922	100923	<LOD	<LOD	<LOD	<LOD	<LOD
110929	110930	1.48	5.29	28.75	2.97	14.41
110930	111003	2.72	<LOD	<LOD	4.70	0.85
111005	111006	<LOD	7.82	19.62	<LOD	16.50
111007	111010	<LOD	<LOD	<LOD	1.36	1.46
111011	111018	<LOD	<LOD	<LOD	<LOD	<LOD
111026	111028	<LOD	<LOD	24.37	10.53	<LOD