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Acidic reaction products of monoterpenes and sesquiterpenes in atmospheric fine particles in a boreal forest

M. Vestenius[1], **H. Hellén**[1], **J. Levula**[2], **P. Kuronen**[1], **K.J. Helminen**[3], **T. Nieminen**[2], **M. Kulmala**[2], **and H. Hakola**[1]

[1]Finnish Meteorological Institute, Atmospheric Composition Research, P.O. Box 503, 00101 Helsinki, Finland
[2]Department of Physics, P.O. Box 64, University of Helsinki, 00014 Helsinki, Finland
[3]Department of Chemistry, P.O. Box 55, University of Helsinki, 00014 Helsinki, Finland

Correspondence to: M. Vestenius (mika.vestenius@fmi.fi)

Abstract. Biogenic acids were measured in aerosols at the SMEAR II (Station for Measuring Forest Ecosystem-Atmosphere Relations II) station in Finland from June 2010 until October 2011. The analysed organic acids were pinic, pinonic, caric, limonic and caryophyllinic acids from oxidation of α-pinene, β-pinene, limonene, Δ^3-carene and β-caryophyllene, respectively. Due to a lack of authentic standards, the caric, limonic and caryophyllinic acids were synthesised for this study. The mean, median, maximum and minimum concentrations (ng m^{-3}) were as follows: limonic acid (1.26, 0.80, 16.5, below detection limit ($<$ LOD)), pinic acid (5.53, 3.25, 31.4, 0.15), pinonic acid (9.87, 5.07, 80.1, $<$ LOD), caric acid (5.52, 3.58, 49.8, $<$ LOD), and caryophyllinic acid (7.87, 6.07, 86.1, $<$ LOD).

The highest terpenoic acid concentrations were measured during the summer. Of the acids, β-caryophyllinic acid showed the highest concentrations in summer, but during other times of the year pinonic acid was the most abundant. The β-caryophyllinic acid contribution was higher than expected, based on the emission calculations of the precursor compounds and yields from oxidation experiments in smog chambers, implying that the β-caryophyllene emissions or β-caryophyllinic acid yields were underestimated. The concentration ratios between terpenoic acids and their precursors were clearly lower in summer than in winter, indicating stronger partitioning to the aerosol phase during the cold winter season. The β-caryophyllinic and caric acids were weakly correlated with the accumulation-mode particle number concentrations.

1 Introduction

Large amounts of biogenic volatile organic compounds (BVOCs) (isoprene, monoterpenes and sesquiterpenes) are emitted into the atmosphere by vegetation, especially in the densely forested boreal regions (Hakola et al., 2001, 2006; Tarvainen et al., 2005, 2007; Hellén et al., 2006; Wiedinmyer et al., 2004; Steiner and Goldstein, 2007). In the atmosphere, these compounds are oxidised, resulting in reaction products, e.g. acids and carbonyl-containing compounds that participate in the formation and growth of new particles (Kulmala et al., 2004; Tunved et al., 2006). Current estimates suggest that global biogenic secondary organic aerosol (SOA) sources are larger than anthropogenic sources (Hallquist et al., 2009). Even though organic compounds account for 20–90 % of the total fine particle mass concentration in a wide variety of atmospheric environments (Kanakidou et al., 2005), little information is available on their detailed composition.

In smog chamber studies, the SOA yields for the various hydrocarbons and even for the monoterpenes vary considerably (Griffin et al., 1999; Yu et al., 1999; Jaoui et al., 2003; Lee et al., 2006). The produced compounds have very different vapour pressures, and partitioning between the gas and aerosol phases varies widely. Detailed knowledge of the occurrence of individual compounds is therefore 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 for Measuring Forest Ecosystem-Atmosphere Relations II; Hari and Kulmala, 2005) station in Finland from June 2010 until October 2011.

2 Experiments

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 was 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 hydrocar-

bons 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 PM_{10} 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 1 ml of 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 ionisation 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, 2.1×150 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 programme 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 the sensitivity of the instrument. The concentrations of the analytes in the samples varied between below the 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
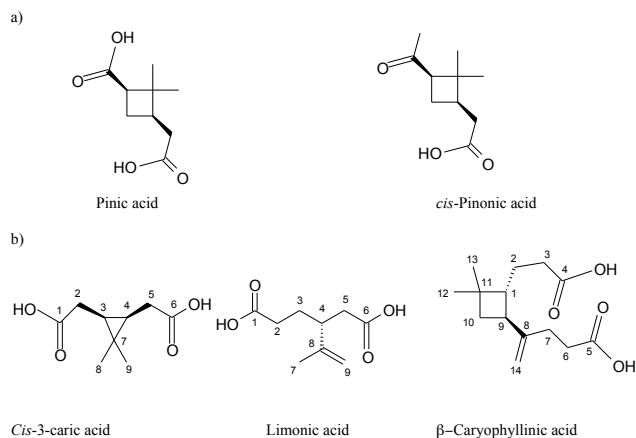
Figure 1. Structures of **(a)** commercially available and **(b)** synthesised terpenoic acids. The numbers refer to the C atoms in the NMR spectra.

(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 the 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 synthesised 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 ionisation-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 recrystallisation from cyclohexane–toluene–isopropanol to give a white powder with a 10 % overall yield and 95 % purity (estimated by NMR); Mp. (Melting point) 109–112 °C (in literature 112–113 °C; Semmler and von Schiller, 1927). ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 12.22 (br, 2H, 1 and 6

COOH), 2.62 (dd, J = 17 Hz, 3.5 Hz, 2H, 2 and 5), 2.03 (m, 2H, 2 and 5), 1.04 (s, 3H, 8), 1.01 (m, 2H, 3 and 4), 0.92 (s, 3H, 9); ^{13}C NMR (CDCl$_3$, 126 MHz) δ: 180.9 (1 and 6), 30.2 (2 and 5), 28.5 (8), 22.0 (3 and 4), 17.3 (7), 15.4 (9). The high-resolution MS (HRMS) (ESI-TOF) mass-to-charge ratio (m/z), calculated for C$_9$H$_{14}$NaO$_4$ (M+Na) 209.0784, found 209.0788. IR attenuated total reflection (ATR) ν: 3013 cm^{-1}, 2992 cm^{-1}, 2919 cm^{-1}, 2868 cm^{-1}, 2849 cm^{-1}, 2655 cm^{-1}, 2620 cm^{-1}, 2591 cm^{-1}, 2551 cm^{-1}, 1694 cm^{-1}, 941 cm^{-1}, 923 cm^{-1}, 905 cm^{-1}.

Limonic acid was prepared, starting from (R)-limonene (Aldrich, 97 % purity), which was epoxidised with *meta*-chloroperbenzoic acid (Aldrich, 85 %) and NaHCO$_3$ in dichloromethane (DCM) to limonene epoxide (Naves and Grampoloff, 1961). Oxidative ring opening of the epoxide with NaIO$_4$ (Aldrich, 99.8 %) in water–tetrahydrofuran (THF) (Cane et al., 1992) resulted in limonon aldehyde, which was oxidised with NaClO$_2$ (Aldrich, 80 %) in dimethyl sulphoxide (DMSO) (Binder et al., 2008) to limononic acid. The ketoacid was esterified with ethyl bromide and NaHCO$_3$ in DMSO (Bocchi et al., 1979), and purified by flash chromatography (solvent gradient from pentane to 1 : 1 Et$_2$O-pentane) to give ethyl limononate as a colourless oil. Thin-layer chromatography (TLC) r$_F$: 0.37 (EtOAc:hexane 1 : 2, vanillin staining). ^{1}H NMR (CDCl$_3$, 500 MHz) 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 and 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, 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), 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 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}, 1731 cm^{-1}, 1715 cm^{-1}, 1646 cm^{-1}, 894 cm^{-1}.

Haloform reaction of ethyl limononate with NaOBr in dioxane/water (Staunton and Eisenbraun, 1973) yielded limonic acid, which was purified by flash chromatography on silica (solvent gradient from 50:1 CHCl$_3$–AcOH to 5:45:1 MeOH–CHCl$_3$–AcOH) to give a white solid with a 24 % yield (based on limonene) and 97 % purity (estimated by NMR). Mp. 115–117 °C (in literature 117–118 °C; Abe, 1943). $[\alpha]_D^{22,6}$ = +7.416 (c = 0.5, *i*-PrOH). ^{1}H NMR (acetone-d6, 500 MHz) δ: 10.48 (br, 2H, 1 and 6 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), 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: 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 (ESI-TOF) m/z, calculated for C$_9$H$_{14}$NaO$_4$ (M+Na) 209.0784, found 209.0780. IR (ATR) ν: 3081 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 cm^{-1}.
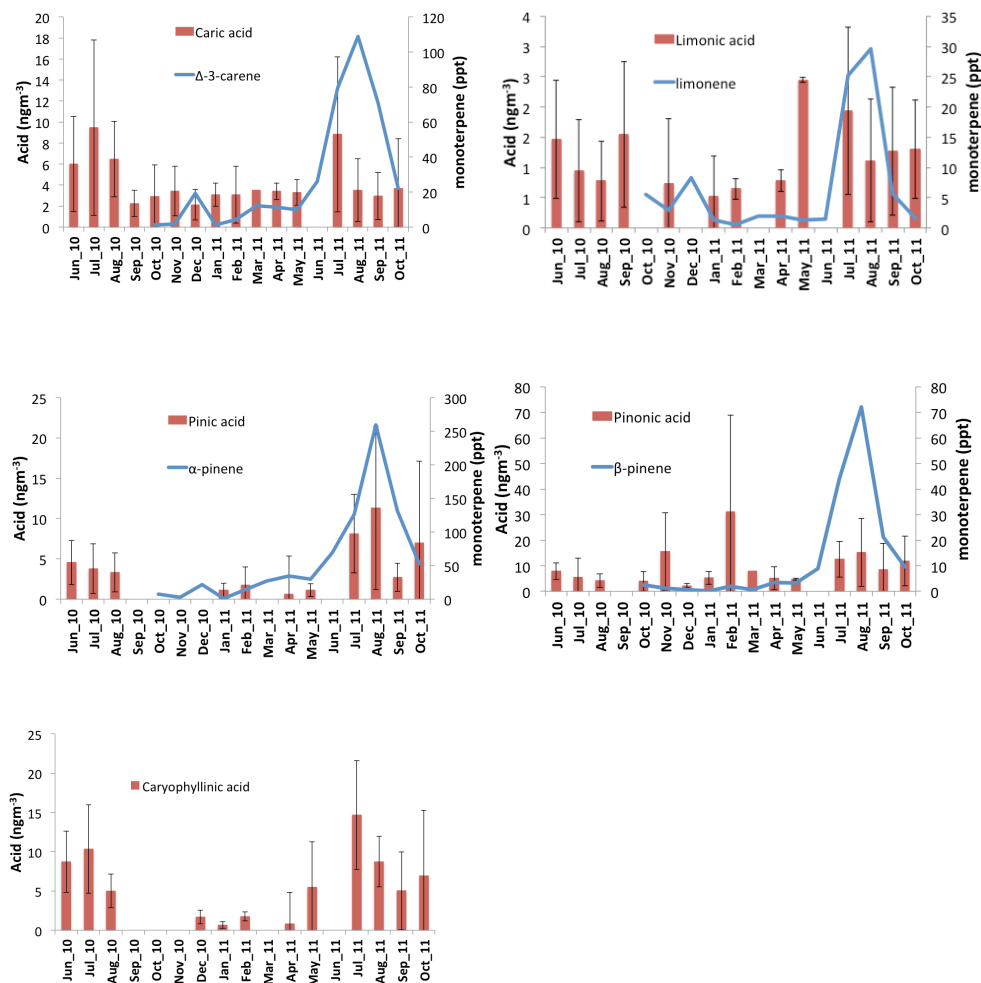
Figure 2. Monthly mean terpenoic acid concentrations and their standard deviations together with monthly mean monoterpene concentrations from Hakola et al. (2012).

β-caryophyllinic acid was prepared from β-caryophyllene oxide (Aldrich, 99 % purity) by a method that will be published separately. It was obtained as a glassy solid of >98 % purity after flash chromatography on silica (solvent gradient from 50:1 $CHCl_3$–AcOH to 5:45:1 MeOH–$CHCl_3$–AcOH); TLC r_F 0.62 (10:90:2 MeOH–DCM–AcOH, Ce–phosphomolybdate staining). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 10.89 (br, 4 and 5 COOH), 4.76 (s, 1H, 14), 4.72 (s, 1H, 14), 2.50 (t, J = 7.7 Hz, 2H, 6), 2.42 (q, J = 9.3 Hz, 1H, 9), 2.35-2.22 (m, 4H, 3 and 7), 1.94 (dt, J = 9.2, 7.7 Hz, 1H, 1), 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), 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), 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), 22.4 (13). HRMS (EI), derivatisation with N,O–bis(trimethylsilyl)trifluoroacetamide (BSTFA) to bis-trimethylsilyl ester, m/z, calculated for $C_{20}H_{38}O_4Si_2(M^+)$ 398.2327, found 398.2318. EI-MS (70

eV) m/z (%): 400 (3), 399 (4), 398 (12) [M], 385 (6), 384 (13), 383 (50) [M–CH_3], 355 (8) [M–CH_3–CO], 328 (7) [M–C_5H_{10}], 313 (26), 309 (100), 299 (37), 279 (19), 200 (81) [M–2(C_5H_{10})], 149 (67) 117 (85).

3 Results and discussion

3.1 Annual variability of terpenoic acids

The highest terpenoic acid concentrations were measured during summer (Fig. 2), but high concentrations, especially of pinonic acid, were also measured occasionally during winter. 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. Reactions with nitrate radicals at least are fast enough to produce acids in less than half an hour (Hakola et al.,

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 / Δ^3-carene	12	5.7	1.5	2.6
PM_1 ($\mu g\,m^{-3}$)	4.8	3.1	5.3	2.9

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 the 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 a few birches growing in the area, and birches emit limonene in 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 the sampling time, but no clear correlations were found. Averaging over the whole day or several days complicates this inspection.

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.

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.

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.

3.2 Comparison of terpenoic acids with corresponding monoterpenes

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. A detailed description of the monoterpene measurements can be found in Hakola et al. (2012). In Fig. 2, we compared the BVOC mixing ratios with the corresponding acid concentrations and

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	PM$_{2.5}$	Warnke et al. (2006)
Mar/Apr 11	0.66–7.3	0.5–11	PM$_{2.5}$	This study
Summer				
Jul/Aug 01	0.38–4.7	0.91–8.2	PM$_{2.5}$	Warnke et al. (2006)
Jul/Aug 05	2–29.6		PM$_{1}$	Kourtchev et al. (2008)
Aug 07	1–7	11–28	PM$_{2.5}$	Parshintsev et al. (2010)
Jul/Aug 10/11	0.64–31	0.1–80	PM$_{2.5}$	This study

found that the overall seasonal patterns were similar, although not all the acid peaks were seen in the parent monoterpene data. This was expected, since the measurement times of the VOCs and corresponding acids did not cover whole months and did not always match. In the online VOC measurements, there were several breaks due to malfunction of the instrument, and because the sampling times of the acids were sometimes several days, the overlapping of VOC and acid data is not complete. Comparisons of these seasonal means thus represent approximations only. However, since the daily variation in VOC mixing ratios is quite modest compared with the seasonal variability, comparing VOC and acid concentrations is justified. The seasonal means of the acid and monoterpene concentrations and the ratios between the acids and precursor monoterpenes are tabulated in Table 1.

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

Tarvainen et al. (2007) calculated the BVOC emissions in the middle boreal zone in Finland, utilising satellite land-cover information, meteorological data and published emission factors in a Biogenic Emissions Inventory System (BEIS)-type canopy emission model. They did not calculate the emissions for β-caryophyllene, but rather for total sesquiterpenes. However, in the published sesquiterpene emission rates (Hakola et al., 2006; Tarvainen et al., 2005), β-caryophyllene was clearly the predominant sesquiterpene species emitted in boreal forests. We compared these emissions with the corresponding acid concentrations (Fig. 3) and found that they were in relatively good agreement. The pinic and pinonic acids and the α- and β-pinenes are added together, since both of these monoterpenes produce both acids. The caric and limonic acids showed lower contributions than their precursors in the emission calculations. This was expected, since their yields in the smog chamber experiments

were lower than the yields of the other acids (Yu et al., 1999; Jaoui et al., 2006, 2003). However, the yield of β-caryophyllinic acid (Jaoui et al., 2003) was also lower than the pinic and pinonic acid yields, but its contribution was higher than expected, based on the emission calculations, especially since the calculations also included other sesquiterpenes. This could imply that the β-caryophyllene emissions or β-caryophyllinic acid yields were underestimated.

3.3 Comparison with particulate data

The highest seasonal means for PM$_{1}$ were observed in summer, together with the highest terpenoic acid concentrations (Table 1), but the measured terpenoic acids explained only a small fraction of the total PM$_{1}$ mass: 0.2 % in winter and 0.7 % in summer.

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

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}
100 604	100 607	0.71	4.86	8.10	2.27	10.25
100 607	100 609	1.10	< LOD	7.18	5.96	6.40
100 609	100 611	1.62	0.52	11.35	14.87	12.44
100 611	100 614	0.35	2.64	13.68	1.07	13.79
100 614	100 616	2.45	7.28	6.77	9.10	13.50
100 616	100 618	1.98	< LOD	3.12	4.42	< LOD
100 621	100 623	0.33	7.29	8.91	1.36	5.47
100 628	100 630	1.41	4.94	4.01	5.25	5.45
100 630	100 702	3.24	7.28	8.02	9.72	8.10
100 705	100 707	< LOD	< LOD	< LOD	21.13	18.77
100 707	100 709	< LOD	< LOD	< LOD	23.69	14.09
100 709	100 712	< LOD	< LOD	< LOD	< LOD	< LOD
100 716	100 719	< LOD	< LOD	< LOD	4.37	5.41
100 719	100 721	< LOD	< LOD	< LOD	2.43	< LOD
100 723	100 726	2.08	5.77	2.46	9.30	8.89
100 726	100 728	1.29	2.34	8.50	6.27	10.36
100 729	100 730	1.46	8.53	23.21	6.73	16.05
100 730	100 802	0.72	1.78	2.22	2.22	3.67
100 802	100 804	1.97	7.28	7.35	9.39	6.13
100 804	100 806	0.88	3.49	5.74	7.59	8.82
100 806	100 809	0.74	4.86	2.07	2.25	4.14
100 811	100 813	< LOD	< LOD	6.72	10.80	2.96
100 813	100 816	< LOD	< LOD	< LOD	6.59	4.27
100 915	100 922	2.39	< LOD	< LOD	3.13	< LOD
100 922	100 930	< LOD	< LOD	< LOD	1.38	< LOD
101 004	101 011	< LOD	< LOD	< LOD	< LOD	< LOD
101 025	101 101	< LOD	< LOD	6.68	5.03	< LOD
101 108	101 119	1.98	< LOD	32.99	5.16	< LOD
101 119	101 122	< LOD	< LOD	8.27	4.43	< LOD
101 122	101 129	0.15	0.15	5.50	0.74	1.30
101 129	101 207	< LOD	< LOD	2.55	3.74	0.68
101 213	101 220	< LOD	< LOD	< LOD	1.68	< LOD
101 227	110 103	< LOD	< LOD	< LOD	< LOD	< LOD
110 103	110 110	1.47	2.12	8.65	4.05	1.15
110 110	110 117	< LOD	< LOD	4.33	2.86	< LOD
110 118	110 125	< LOD	< LOD	2.78	3.77	< LOD
110 125	110 201	0.50	< LOD	5.20	1.60	< LOD
110 201	110 207	0.53	0.17	4.24	5.01	1.34
110 214	110 221	< LOD	< LOD	57.87	1.17	< LOD
110 228	110 307	< LOD	< LOD	4.40	2.50	< LOD
110 328	110 404	1.04	7.28	11.39	4.53	6.47
110 426	110 502	0.78	< LOD	5.09	3.41	0.79
110 502	110 509	2.42	< LOD	4.45	2.44	1.36
110 516	110 524	2.48	1.70	5.06	4.16	9.56
110 630	110 701	3.71	29.37	35.21	18.10	30.84
110 701	110 704	16.46	16.06	80.14	49.78	86.09
110 704	110 705	0.55	21.85	23.03	0.98	7.83
110 705	110 706	1.83	< LOD	23.02	4.47	7.25
110 706	110 706	< LOD	0.00	< LOD	14.99	< LOD
110 711	110 712	5.75	9.17	9.94	28.66	32.68
110 712	110 713	< LOD	10.98	< LOD	0.91	< LOD
110 713	110 714	< LOD	14.48	< LOD	< LOD	< LOD
110 714	110 715	< LOD	< LOD	< LOD	1.55	< LOD
110 715	110 718	1.21	< LOD	< LOD	4.74	7.33

Table 3. Continued.

| 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}
110 718	110 719	< LOD	< LOD	< LOD	3.14	< LOD
110 719	110 720	1.05	< LOD	20.64	7.59	12.38
110 720	110 721	1.24	< LOD	7.38	12.49	14.96
110 721	110 722	< LOD	< LOD	< LOD	8.29	8.17
110 725	110 726	0.87	< LOD	11.08	2.47	6.70
110 726	110 727	< LOD	5.35	< LOD	2.61	< LOD
110 728	110 729	1.02	16.55	12.85	3.16	13.50
110 729	110 801	0.89	< LOD	4.59	3.96	5.61
110 801	110 802	< LOD	20.71	12.70	1.86	10.84
110 802	110 803	1.82	13.81	19.38	0.53	11.06
110 804	110 805	< LOD	< LOD	22.65	8.56	11.05
110 805	110 808	0.81	< LOD	< LOD	4.59	5.17
110 808	110 809	0.94	15.22	5.88	0.99	9.78
110 809	110 810	1.33	20.56	28.95	1.06	11.65
110 811	110 812	< LOD	< LOD	< LOD	6.74	9.34
110 815	110 816	3.37	31.40	43.34	3.25	12.15
110 816	110 817	2.27	< LOD	20.11	8.03	6.02
110 818	110 819	< LOD	< LOD	10.30	0.88	< LOD
110 826	110 829	0.30	< LOD	< LOD	2.25	< LOD
110 901	110 907	2.81	4.03	3.35	5.23	5.78
110 909	110 912	2.11	< LOD	9.65	6.00	4.66
110 916	110 919	< LOD	< LOD	< LOD	1.92	< LOD
110 919	110 921	< LOD	< LOD	< LOD	1.18	< LOD
100 922	100 923	< LOD	< LOD	< LOD	< LOD	< LOD
110 929	110 930	1.48	5.29	28.75	2.97	14.41
110 930	111 003	2.72	< LOD	< LOD	4.70	0.85
111 005	111 006	< LOD	7.82	19.62	< LOD	16.50
111 007	111 010	< LOD	< LOD	< LOD	1.36	1.46
111 011	111 018	< LOD	< LOD	< LOD	< LOD	< LOD
111 026	111 028	< LOD	< LOD	24.37	10.53	< LOD
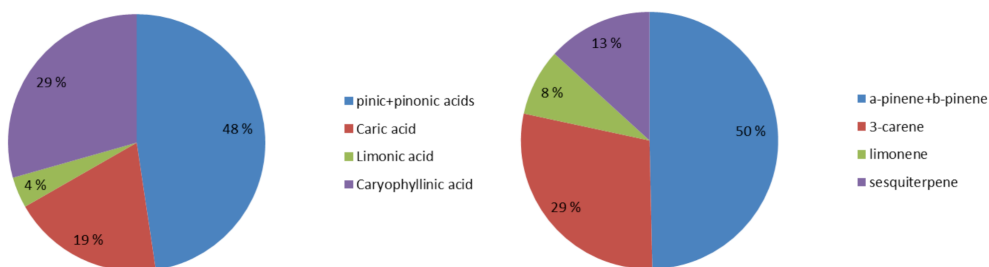
Figure 3. Relative contributions of terpenoic acids in summer (left) and average terpenoid emission fluxes (right) from middle boreal zone forests in summer from Tarvainen et al. (2007).

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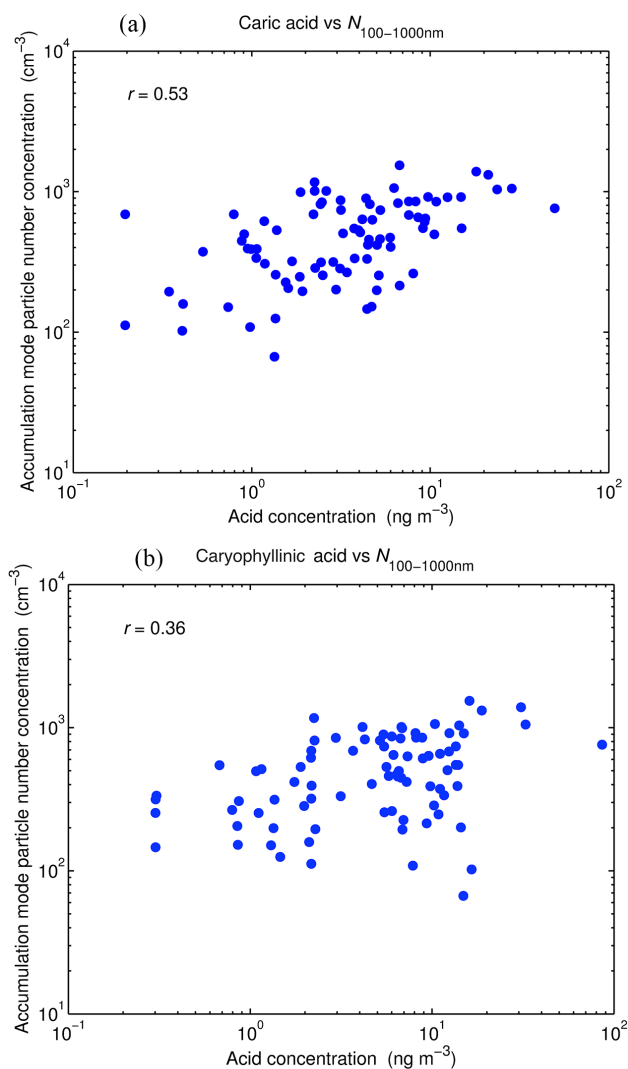
Figure 4. Correlations between caric acid (**a**) and β-caryophyllinic acid (**b**) and the accumulation-mode particle number concentrations.

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 ($\sim$ 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, im-

plying that they participated in the particle growth process, which is crucial for the formation of cloud condensation nuclei.

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