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

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Abstract

Biogenic acids were measured from PM_{2.5} aerosols at SMEAR II station (Station For Measuring Forest Ecosystem-Atmosphere Relations) in Finland from June 2010 until October 2011. The measured organic acids were pinic, pinonic, caric, limonic and caryophyllinic acids from oxidation of α -pinene, β -pinene, limonene, $\Delta 3$ -carene and β -caryophyllene. Due to lack of authentic standards caric, limonic and caryophyllinic acids were synthesized at the Laboratory of Organic Chemistry, University of Helsinki.

The highest terpenoic acid concentrations were measured during summer concomitant with the precursor mono- and sesquiterpenes. Of the acids β -caryophyllinic acid had 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 on the basis of emission calculations of precursor compounds and yields in oxidation experiments in smog chambers implicating that β -caryophyllene emissions or β -caryophyllinic acid yields are underestimated. Concentration ratios between terpenoic acids and their precursor were clearly lower in summer than in winter indicating stronger partitioning to the aerosol phase during cold winter season. The β -caryophyllinic and caric acids were correlated with the accumulation mode particle number concentrations.

1 Introduction

A large amount of biogenic VOCs (isoprene, monoterpenes and sesquiterpenes) is emitted to 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 oxidized producing reaction products e.g. acids and carbonyls, which take part 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

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(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), only little is known about their detailed composition.

5 In smog chamber studies the secondary organic aerosol (SOA) yields for different hydrocarbons and even for different monoterpenes have been found to vary considerably (Griffin et al., 1999; Yu et al., 1999; Jaoui et al., 2003; Lee et al., 2006). Produced compounds have very different vapor pressures and partitioning between gas and aerosol phases varies a lot. Therefore detailed knowledge of individual compounds is essential
10 for the atmospheric studies.

There are some studies on concentrations of 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 is known on concentrations of other terpenoic acids mainly
15 due to the lack of authentic standards. In some studies concentrations of other terpenoic acids have been estimated by indirect calibration methods (Gomez-Gonzalez et al., 2012; Fu et al., 2009; Warnke et al., 2006). Especially products of sesquiterpenes are of interest since the parent compounds are often too reactive to be measured in ambient air. β -Caryophyllene has been found to be the main sesquiterpene in many
20 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 because of its reactivity and high aerosol yields found in smog chamber studies (Jaoui et al., 2003; Lee et al., 2006; Chen et al., 2012).

In this study the reaction products of biogenic VOCs, which affect the formation and
25 growth of fine particles, were analyzed from aerosol samples taken at the SMEAR II station (Station For Measuring Forest Ecosystem-Atmosphere Relations; Hari and Kulmala, 2005) in Finland from June 2010 until October 2011.

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2 Experimental

2.1 Sampling

The measurements were conducted at the SMEAR II station (Station For Measuring Forest Ecosystem-Atmosphere Relations 61°51' N, 24°18' E, 181 m a.s.l.) at Hytylä, in southern Finland (Hari and Kulmala 2005). The largest nearby city is Tampere with 200 000 inhabitants. It is located 60 km to the south-west of the site. The nearest vegetation is a homogeneous Scots pine forest with some birches and Norway spruces growing nearby.

The aerosol samples were collected using pumped sampling from June 2010 until
10 October 2011, from the PM_{2.5} fractions in air on to quartz filters (Pallflex Tissuquartz 2500QAT-UP, i.d. 47 mm). Total of 86 samples were collected. Before sampling filters were heated to 600 °C for over 8 h. Occasionally we used an additional back-up filter, but no breakthrough was observed. Air flow through the filters was 16 L min⁻¹. Collection times were 1–7 days per filter. The sampling dates and times are shown in the
15 Table A1. Longer, 7 days samples were collected during winter due to expected low concentrations. Gases were removed from the air flow before the filters using parallel plate carbon denuder (Sunset Laboratory Inc.). Efficiency of the denuder was checked by taking samples of more volatile organic compounds (aromatic hydrocarbons and monoterpenes) than measured in this study using pumped adsorbent sampling.

2.2 Sample preparation and analysis

Samples were extracted into 50 mL of methanol (J. T. Baker 8402) using ultrasonic bath for 90 min and then evaporated into one millilitre volume using Büchi Syncore evaporator and further evaporated into 100 μ L under nitrogen flow. The samples were analyzed using high performance liquid chromatography (Agilent 1100 Series) with electro spray
25 ionisation and ion trap mass spectrometer (Agilent 1100 Series LC/MSD Trap). The column used was Waters Xterra[®] MS C18 (3.5 μ m, 2.1 \times 150 mm). The main compo-

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ments of the mobile phase were MilliQ water and acetonitrile. The pH of the mobile phase was adjusted to ~ 3 with acetic acid. The 80 min long gradient program started with 95 % of water and 5 % ACN and from 5 min ACN was gradually increased to 8 % at 10 min. After 10 min the ACN concentration was held at 8 % until 40 min, thereafter it was fast increased to 90 % at the point of 45 min and to 95 % at the point of 50 min. The concentration was then held constant until 70 min, after that it was dropped into 5 % at the point of 71 min and held at 5 % until the end of the run. The column was held at the constant temperature of 65 °C. The samples were analysed using external standards at four-point calibration curve. Camphoric acid was used as a internal standard in order to correct the losses in sample preparation, matrice effects and changes in sensitivity of the instrument. Concentrations of the analytes in samples varied between 0.05 to 145 ng m⁻³. The limit of detection was calculated using the standard deviation of the blank samples and it was typically from 0.1 to 0.8 ng m⁻³. Each of the compounds were measured individually using ion trap detector's scan mode to determine the retention times and representative ions for each compound from standard solution. Then in the analysis runs, the detector was used in multiple reaction monitoring (MRM) mode where each compound was monitored in it's own retention time window using it's 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 forest (Tervainen et al., 2007) for target compounds of the study. Pinic and pinonic acids were commercially available, but β -caryophyllinic acid, *cis*-3-caric acid and limonic acid (Fig. 1) were synthesized at the Laboratory of Organic Chemistry, University of Helsinki.

The description of the syntheses and characterization of the synthesized dicarboxylic acids are as follows:

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NMR spectra were recorded on Varian Unity Inova 500 spectrometer. Mass spectra were obtained with Bruker microTOF (ESI-TOF) or JEOL JMS-700 (EI-MS) instruments. IR spectra were recorded on Bruker Alpha-P FT-IR instrument. Melting points were determined in open capillary tubes with Büchi B-545 apparatus.

Cis-3-caric acid was prepared from delta-3-carene (Aldrich, 95 % purity) by RuCl₃-catalyzed oxidation with NaIO₄ (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-isopropanol to give white powder in 10 % overall yield and 95 % purity (estimated by NMR). Mp. 109–112 °C (lit. 112–113 °C, Semmler and von Schiller, 1927). ¹H NMR (CDCl₃, 500 MHz) δ : 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, 3H, 8), 1.01 (m, 2H, 3 & 4), 0.92 (s, 3H, 9); ¹³C NMR (CDCl₃, 126 MHz) δ : 180.9 (1 & 6), 30.2 (2 & 5), 28.5 (8), 22.0 (3 & 4), 17.3 (7), 15.4 (9). HRMS (ESI-TOF) *m/z* calcd for C₉H₁₄NaO₄ (M + Na) 209.0784, found 209.0788. IR (ATR) *v*: 3013, 2992, 2919, 2868, 2849, 2655, 2620, 2591, 2551, 1694, 941, 923, 905.

Limonic acid was prepared starting from (*R*)-limonene (Aldrich, 97 % purity), which was epoxidized with meta-chloroperbenzoic acid (Aldrich, 85 %) and NaHCO₃ in dichloromethane to limonene epoxide (Naves and Grampoloff, 1961). Oxidative ring opening of the epoxide with NaIO₄ (Aldrich, 99.8 %) in water-THF (Cane et al., 1992) gave limononaldehyde, which was oxidized with NaClO₂ (Aldrich, 80 %) in DMSO (Binder et al., 2008) to limononic acid. The ketoacid was esterified with ethyl bromide and NaHCO₃ in DMSO (Bocchi et al., 1979) and purified by flash chromatography (solvent gradient from pentane to 1 : 1 Et₂O-pentane) to give ethyl limononate as a colorless oil. TLC *rF*: 0.37 (EtOAc : hexane 1 : 2, vanillin staining). ¹H NMR (CDCl₃, 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 & 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); ¹³C 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),

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26.4 (4), 18.5 (8), 14.3 (12). HRMS (ESI-TOF) m/z calcd for $C_{12}H_{20}NaO_3$ (M + Na) 235.1305, found 235.1313. IR (ATR) ν : 3075, 2982, 2937, 1731, 1715, 1646, 894.

Haloform reaction of ethyl limononate with NaOBr in dioxane/water (Staunton and Eisenbraun, 1973) afforded limonic acid, which was purified by flash chromatography on silica (solvent gradient from 50 : 1 CHCl₃-AcOH to 5 : 45 : 1 MeOH-CHCl₃-AcOH) to give white solid in 24 % yield (based on limonene) and 97 % purity (estimated by NMR). Mp. 115–117 °C (lit. 117–118 °C, Abe, 1943). $[\alpha]D_{22,6} = +7.416$ ($c = 0.5$, i-PrOH). ¹H NMR (acetone-d₆, 500 MHz) δ : 10.48 (br, 2H, 1 & 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); ¹³C 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 calcd for $C_9H_{14}NaO_4$ (M + Na) 209.0784, found 209.0780. IR (ATR) ν : 3081, 2976, 2941, 2911, 2668, 2573, 1699, 1694, 1647, 896.

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 CHCl₃-AcOH to 5 : 45 : 1 MeOH-CHCl₃-AcOH). TLC rF 0.62 (10 : 90 : 2 MeOH-DCM-AcOH, Ce-phosphomolybdate staining). ¹H NMR (CDCl₃, 500 MHz) δ : 10.89 (br, 4 & 5 COOH), 4.76 (s, 1H, 14), 4.72 (s, 1H, 14), 2.50 (t, $J = 7.7$ 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), 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); ¹³C NMR (CDCl₃, 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), derivatization with BSTFA to bis-trimethylsilyl ester, m/z calcd 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-CH₃], 355 (8) [M-CH₃-CO], 328 (7) [M-C₅H₁₀], 313 (26), 309 (100), 299 (37), 279 (19), 200 (81) [M-2(C₅H₁₀)], 149 (67) 117 (85).

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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 were measured occasionally also during winter, especially pinonic acid concentrations were sometimes very high. Hakola et al. (2012) measured BVOC concentrations at the same site and found very high BVOC concentrations originating from the nearby sawmills. These emissions are very likely to cause high acid concentrations as well. The results are tabulated in the Table A1 and the Table A1 also shows the length of each measurement. Table 1 shows seasonal average concentrations. β -Caryophyllinic acid had 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 it is expected that also the product concentrations peak then. Limonic acid is spread 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; Tarvainen et al., 2013). The concentrations were also studied in relation to meteorological parameters such as temperature, wind speed, relative humidity and the rain amount of the sampling time, but no clear correlations were found. Averaging over whole day or several days complicates this inspection.

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

Concentrations of pinonic and pinic acids had relatively good correlation during summer months ($r_2 = 0.42$). This was expected since they have same precursors i.e. they

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are both reaction products of α - and β -pinene. Averagely concentrations for pinonic acid were 40 % higher than for pinic acid. Also caric acid and caryophyllinic acid were correlated ($r_2 = 0.47$) in summer.

Pinic and pinonic acids have been measured at SMEAR II station also earlier in short one or two month campaigns in spring and summer. Results from earlier studies are listed in Table 2. Kourtchev et al. (2008) measured pinic acid in July–August 2005 in PM_{1} fraction and found the median value of 7.7 ng m^{-3} which is very close to the summer median in our measurements (6.7 ng m^{-3}). Also other earlier results were in same range as our values.

10 3.2 Comparison of terpenoic acids with corresponding monoterpenes

Ambient monoterpene concentrations were measured at the same site from October 2010 until November 2011 close to the filter sampling site by in-situ gas chromatograph-mass spectrometer. Detailed description of the monoterpene measurements can be found in Hakola et al. (2012). In the Fig. 3 we compared the BVOC mixing ratios with corresponding acid concentrations and found that the overall seasonal patterns are similar although not all acid peaks are seen in the parent monoterpene data. This is expected since the measurement times of VOCs and corresponding acids did not cover whole months and most of the time they were not matching. Thus comparing these monthly means represents approximates only. The monthly means of the acid and monoterpene concentrations and the ratios between the acids and precursor monoterpenes are tabulated in Table 1.

Jaoui and Kamens (2003) conducted chamber experiments with α -pinene and β -pinene during daytime (OH initiated reaction) and nighttime with ozone addition. They found pinic acid and pinonic acid in aerosol phase with about 6.4 % and 4.7 % yields in nighttime reactions and 5.9 % and 3.7 % in daytime reactions, respectively. In our measurements, and also in the measurements by Warnke et al. (2006), the contribution of pinonic acid was larger than that of pinic acid contrary to the chamber experiments. In A3-carene ozone oxidation reaction the main acid produced in aerosol phase is

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3-caronic acid (1.5 %) and caric acid (1.3 %) (Yu et al., 1999). Jaoui et al. (2006) identified limonic acid in limonene ozone oxidation reaction with 0.14 % yield and Jaoui et al. (2003) identified β -caryophyllinic acid totally in aerosol phase with 4 % yield. In our study concentration ratios between terpenoic acids and their precursor were between 0.5 and 17 % and clearly lower in summer than in winter (Table 1). This suggests that during the cold seasons the acids are partitioning more to the particle phase than into the gas phase and visa versa. Temperature, together with carbon and oxygen numbers, are known to be controlling factors in phase partitioning of organic acids (Finlayson-Pitts and Pitts, 2000).

10 Tarvainen et al. (2007) calculated the BVOC emissions in the middle boreal zone in
 Finland utilizing satellite land cover information, actual meteorological data and published emission factors in a BEIS-type canopy emission model. They did not calculate emissions for β -caryophyllene, but for total sesquiterpenes. However, in the published sesquiterpene emission rates (Hakola et al., 2006; Tarvainen et al., 2005) β -caryophyllene is clearly the dominant sesquiterpene species emitted in the boreal forest. We compared these emissions with the corresponding acid concentrations (Fig. 4) and found them to be in quite good agreement. Pinic and pinonic acids and α - and β -pinenes are taken as sums, since both of these monoterpenes produce both acids. Caric and limonic acids have lower contributions than their precursors in the emission 15 calculations. This is expected since their yields in smog chamber experiments are lower than yields of other acids (Yu et al., 1999; Jaoui et al., 2003, 2006). However, also yield of the β -caryophyllinic acid (Jaoui et al., 2003) is lower than pinic and pinonic acid yield, but its contribution is higher than expected on the basis of emission calculations, especially since the calculations include also other sesquiterpenes. This could implicate 20 that β -caryophyllene emissions or β -caryophyllinic acid yields are underestimated.

3.3 Comparison with particulate data

PM₁ concentrations were measured using Dekati PM₁₀ impactor 30LPM version at the same site and same time period as terpenoic acids. It is a three-stage cascade

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impactor which classifies particles into four size fractions with cut-sizes of 10, 2.5 and 1 micrometers. Highest seasonal means for PM_1 were observed in summer together with the highest terpenoic acid concentrations (Table 1). Measured terpenoic acids explained 0.2 % of the total PM_1 mass in winter and 0.7 % in summer.

5 Average submicrometer organic carbon (OC) concentration in Hyttiälä 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). Sum of terpenoic acids measured in this study comprise only 0.9–3.4 %
 of this OC having highest fraction in summer and lowest in winter. Although measure-
 ments were conducted in different years, we can expect that these five terpenoic acids
 10 have only small impact on total OC concentrations especially in winter. However, this
 fraction is clearly higher than 0.6 % for 12 terpenoic acids found by Gomez-Gonzalez
 et al. (2012) in summer in a Belgian forest site.

The acid concentrations were also studied in relation to the particle concentrations in different size fractions. Particle number concentrations were measured in size range 15 3–1000 nm with a DMPS system and 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) caric and caryophyllinic acids were correlated with particle number concentration as shown in Fig. 5. Also PM_1 mass concentration correlated with caric and caryophyllinic acids. Pinic and pinonic acids did 20 not correlate with any particle size fractions. Smog chamber studies have shown that pinonic and pinic acids are partitioning more to the gas phase than other studied acids (Yu et al., 1999).

4 Conclusions

25 The highest terpenoic acid concentrations were measured in summer concomitant 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

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higher than expected on the basis of emission calculations and smog chamber yields implicating that β -caryophyllene emissions or β -caryophyllinic acid yields are underestimated. Limonic acid concentration peaked already in spring. This is in accordance with the measured limonene emissions from spruce that also reach their maximum in spring. Pinonic and limonic acids had quite high concentrations in winter too. These winter concentrations can be of anthropogenic origin. Higher ratios between terpenoic acids and their precursors in winter indicated higher partitioning to aerosol phase during colder winter months.

These five terpenoic acids comprise only small fraction ($\sim 1\text{--}3\%$) of the total organic carbon in particles measured at the site and only 0.2–0.7 % of the PM_{1} mass. The β -caryophyllinic and caric acids were correlated with the accumulation mode particle number concentrations implicating they participate in the particle growth process being important for formation of cloud condensation nuclei.

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Table 1. Seasonal mean concentrations of terpenoic acids from this study and precursor monoterpenes from Hakola et al. (2012) in Hytiälä (June 2010–October 2011), ratios between acids and precursors (%) and mean PM_1 concentrations measured with Dekati PM_{10} impactors in Hytiälä.

	Winter	Spring	Summer	Autumn
Terpenoic acids ($ng\ m^{-3}$)				
Limonic acid	0.6	1.7	1.4	1.1
Pinic acid	1.7	2.6	7.2	3.6
Pinonic acid	4.2	6.5	10.7	8.3
Caric acid	2.6	3.6	7.2	2.9
Caryophyllinic acid	1.2	4.5	10.9	3.8
Monoterpenes ($ng\ m^{-3}$) ($ng\ m^{-3}$)				
α -pinene	40	180	1070	220
β -pinene	4	20	300	40
α -pinene + β -pinene	40	200	1370	260
Δ 3-carene	20	60	480	110
Limonene	10	10	130	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 ($\mu\text{g}\ m^{-3}$)	4.8	3.1	5.3	2.9

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Table 2. Concentrations of pinic and pinonic acids in comparison to earlier studies at SMEAR II station in Hytiälä.

$ng\ m^{-3}$	Pinic acid	Pinonic acid	Particle size	Reference
Spring				
Mar/Apr 2003	1.1–21	0.99–74	$PM_{2.5}$	Warnke et al. (2006)
Mar/Apr 2011	0.66–7.3	0.5–11	$PM_{2.5}$	This study
Summer				
Jul/Aug 2001	0.38–4.7	0.91–8.2	$PM_{2.5}$	Warnke et al. (2006)
Jul/Aug 2005	2–29.6		PM_1	Kourtchev et al. (2008)
Aug 2007	1–7	11–28	$PM_{2.5}$	Parshintsev et al. (2010)
Jul/Aug 2010/2011	0.64–31	0.1–80	$PM_{2.5}$	This study

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Table A1. Sampling times and terpenoic acids 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
4 Jun 2010 13:09	7 Jun 2010 13:05	0.71	4.86	8.10	2.27	10.25
7 Jun 2010 14:06	9 Jun 2010 14:04	1.10	<LOD	7.18	5.96	6.40
9 Jun 2010 14:21	9 Jun 2010 14:20	1.62	0.52	11.35	14.87	12.44
11 Jun 2010 15:19	14 Jun 2010 12:39	0.35	2.64	13.68	1.07	13.79
11 Jun 2010 15:19	14 Jun 2010 12:39	2.45	7.28	6.77	9.10	13.50
16 Jun 2010 09:00	18 Jun 2010 09:00	1.98	<LOD	3.12	4.42	<LOD
21 Jun 2010 12:38	23 Jun 2010 12:38	0.33	7.29	8.91	1.36	5.47
28 Jun 2010 14:39	30 Jun 2010 14:39	1.41	4.94	4.01	5.25	5.45
30 Jun 2010 15:19	2 Jul 2010 15:19	3.24	7.28	8.02	9.72	8.10
5 Jul 2010 15:57	7 Jul 2010 14:32	<LOD	<LOD	<LOD	21.13	18.77
7 Jul 2010 16:15	9 Jul 2010 09:01	<LOD	<LOD	<LOD	23.69	14.09
9 Jul 2010 09:08	12 Jul 2010 09:04	<LOD	<LOD	<LOD	<LOD	<LOD
16 Jul 2010 12:26	19 Jul 2010 12:25	<LOD	<LOD	<LOD	4.37	5.41
19 Jul 2010 14:56	21 Jul 2010 09:02	<LOD	<LOD	<LOD	2.43	<LOD
23 Jul 2010 11:44	26 Jul 2010 10:34	2.08	5.77	2.46	9.30	8.89
26 Jul 2010 12:07	28 Jul 2010 12:06	1.29	2.34	8.50	6.27	10.36
29 Jul 2010 09:05	30 Jul 2010 12:05	1.46	8.53	23.21	6.73	16.05
30 Jul 2010 12:11	2 Aug 2010 12:10	0.72	1.78	2.22	2.22	3.67
4 Aug 2010 09:36	6 Aug 2010 09:35	0.88	3.49	5.74	7.59	8.82
2 Aug 2010 13:09	4 Aug 2010 09:29	1.97	7.28	7.35	9.39	6.13
6 Aug 2010 12:09	9 Aug 2010 12:08	0.74	4.86	2.07	2.25	4.14
11 Aug 2010 16:05	13 Aug 2010 13:34	<LOD	<LOD	6.72	10.80	2.96
13 Aug 2010 13:42	16 Aug 2010 13:41	<LOD	<LOD	<LOD	6.59	4.27
22 Sep 2010 08:09	23 Sep 2010 08:09	2.39	<LOD	<LOD	3.13	<LOD
22 Sep 2010 10:00	30 Sep 2010 10:00	<LOD	<LOD	<LOD	1.38	<LOD
4 Oct 2010 08:00	11 Oct 2010 08:00	<LOD	<LOD	<LOD	<LOD	<LOD
4 Oct 2010 08:00	11 Oct 2010 08:00	<LOD	<LOD	<LOD	<LOD	<LOD
25 Oct 2010 10:00	1 Nov 2010 10:00	<LOD	<LOD	<LOD	<LOD	<LOD
25 Oct 2010 10:00	1 Nov 2010 10:00	<LOD	<LOD	6.68	5.03	<LOD
8 Nov 2010 10:00	19 Nov 2010 10:00	1.98	<LOD	32.99	5.16	<LOD
19 Nov 2010 10:00	12 Jan 2010 10:00	<LOD	<LOD	8.27	4.43	<LOD
22 Nov 2010 10:00	12 Jan 2010 10:00	0.15	0.15	5.50	0.74	1.30
29 Nov 2010 10:00	7 Dec 2010 10:00	<LOD	<LOD	2.55	3.74	0.68
13 Dec 2010 10:00	22 Jan 2010 10:00	<LOD	<LOD	<LOD	1.68	<LOD
27 Dec 2010 09:00	3 Jan 2011 9:00	<LOD	<LOD	<LOD	<LOD	<LOD
3 Jan 2011 09:00	10 Jan 2011 09:00	1.47	2.12	8.65	4.05	1.15
10 Jan 2011 10:00	17 Jan 2011 10:00	<LOD	<LOD	4.33	2.86	<LOD
18 Jan 2011 10:00	25 Jan 2011 10:00	<LOD	<LOD	2.78	3.77	<LOD
25 Jan 2011 10:00	1 Feb 2011 10:00	0.50	<LOD	5.20	1.60	<LOD
1 Feb 2011 13:26	7 Feb 2011 13:19	0.53	0.17	4.24	5.01	1.34
14 Feb 2011 10:00	21 Feb 2011 10:00	<LOD	<LOD	57.87	1.17	<LOD
28 Feb 2011 10:00	7 Mar 2011 10:00	<LOD	<LOD	4.40	2.50	<LOD
28 Mar 2011 09:00	4 Apr 2011 09:00	1.04	7.28	11.39	4.53	6.47

Table A1. 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
26 Apr 2011 10:00	2 May 2011 10:15	0.78	<LOD	5.09	3.41	0.79
2 May 2011 10:21	9 May 2011 10:44	2.42	<LOD	4.45	2.44	1.36
16 May 2011 12:39	24 May 2011 01:55	2.48	1.70	5.06	4.16	9.56
30 Jun 2011 08:29	1 Jul 2011 8:22	3.71	29.37	35.21	18.10	30.84
1 Jul 2011 09:00	4 Jul 2011 09:00	16.46	16.06	80.14	49.78	86.09
4 Jul 2011 08:44	5 Jul 2011 08:29	0.55	21.85	23.03	0.98	7.83
5 Jul 2011 08:29	6 Jul 2011 08:31	1.83	<LOD	23.02	4.47	7.25
6 Jul 2011 08:31	6 Jul 2011 20:15	<LOD	0.00	<LOD	14.99	<LOD
11 Jul 2011 09:45	12 Jul 2011 06:45	5.75	9.17	9.94	28.66	32.68
12 Jul 2011 08:00	12 Jul 2011 08:50	<LOD	10.98	<LOD	0.91	<LOD
13 Jul 2011 08:50	14 Jul 2011 08:35	<LOD	14.48	<LOD	<LOD	<LOD
14 Jul 2011 08:35	15 Jul 2011 08:02	<LOD	<LOD	<LOD	1.55	<LOD
15 Jul 2011 08:02	18 Jul 2011 08:39	1.21	<LOD	<LOD	4.74	7.33
18 Jul 2011 08:39	19 Jul 2011 11:51	<LOD	<LOD	<LOD	3.14	<LOD
19 Jul 2011 11:51	20 Jul 2011 08:58	1.05	<LOD	20.64	7.59	12.38
20 Jul 2011 08:58	21 Jul 2011 10:24	1.24	<LOD	7.38	12.49	14.96
21 Jul 2011 10:24	22 Jul 2011 09:43	<LOD	<LOD	<LOD	8.29	8.17
25 Jul 2011 10:10	26 Jul 2011 08:49	0.87	<LOD	11.08	2.47	6.70
26 Jul 2011 08:49	27 Jul 2011 08:53	<LOD	5.35	<LOD	2.61	<LOD
28 Jul 2011 15:21	29 Jul 2011 10:50	1.02	16.55	12.85	3.16	13.50
29 Jul 2011 10:50	1 Aug 2011 09:05	0.89	<LOD	4.59	3.96	5.61
1 Aug 2011 09:05	2 Aug 2011 08:55	<LOD	20.71	12.70	1.86	10.84
2 Aug 2011 08:55	3 Aug 2011 08:05	1.82	13.81	19.38	0.53	11.06
4 Aug 2011 09:13	5 Aug 2011 08:57	<LOD	<LOD	22.65	8.56	11.05
5 Aug 2011 08:57	8 Aug 2011 08:56	0.81	<LOD	<LOD	4.59	5.17
8 Aug 2011 08:56	9 Aug 2011 08:25	0.94	15.22	5.88	0.99	9.78
9 Aug 2011 08:25	10 Aug 2011 10:51	1.33	20.56	28.95	1.06	11.65
11 Aug 2011 08:40	12 Aug 2011 08:38	<LOD	<LOD	<LOD	6.74	9.34
15 Aug 2011 09:00	16 Aug 2011 08:34	3.37	31.40	43.34	3.25	12.15
16 Aug 2011 08:34	17 Aug 2011 09:04	2.27	<LOD	20.11	8.03	6.02
18 Aug 2011 08:35	19 Aug 2011 08:42	<LOD	<LOD	10.30	0.88	<LOD
26 Aug 2011 08:05	29 Aug 2011 08:50	0.30	<LOD	<LOD	2.25	<LOD
1 Sep 2011 07:40	7 Sep 2011 09:09	2.81	4.03	3.35	5.23	5.78
9 Sep 2011 08:35	12 Sep 2011 07:50	2.11	<LOD	9.65	6.00	4.66
16 Sep 2011 08:59	19 Sep 2011 08:31	<LOD	<LOD	<LOD	1.92	<LOD
19 Sep 2011 08:31	21 Sep 2011 09:30	<LOD	<LOD	<LOD	1.18	<LOD
22 Sep 2011 10:00	23 Sep 2011 10:00	<LOD	<LOD	<LOD	<LOD	<LOD
29 Sep 2011 08:09	30 Sep 2011 08:08	1.48	5.29	28.75	2.97	14.41
30 Sep 2011 08:08	3 Oct 2011 08:30	2.72	<LOD	<LOD	4.70	0.85
5 Oct 2011 08:00	6 Oct 2011 08:30	<LOD	7.82	19.62	<LOD	16.50
7 Oct 2011 09:17	10 Oct 2011 08:25	<LOD	<LOD	<LOD	1.36	1.46
11 Oct 2011 10:00	18 Oct 2011 10:00	<LOD	<LOD	<LOD	<LOD	<LOD
26 Oct 2011 09:43	28 Oct 2011 08:43	<LOD	<LOD	24.37	10.53	<LOD

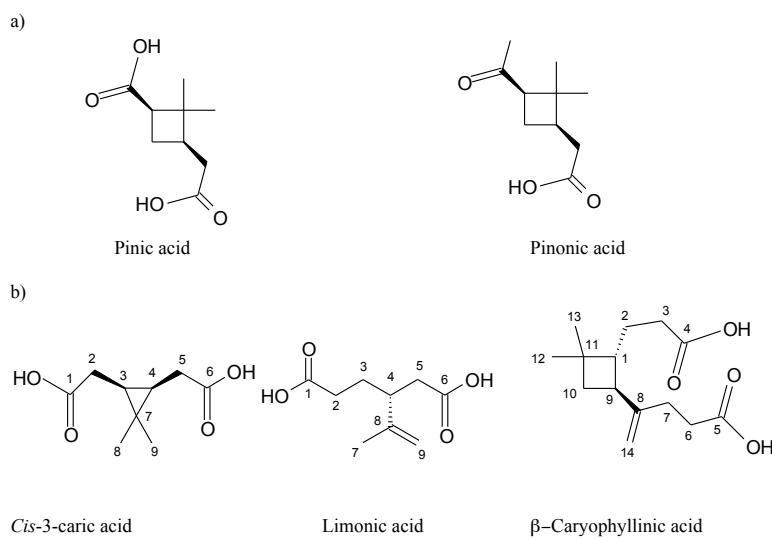


Fig. 1. Structures of (a) the commercially available, (b) the synthesized terpenoic acids. The numbers refer to the C-atoms in the NMR spectra.

2877

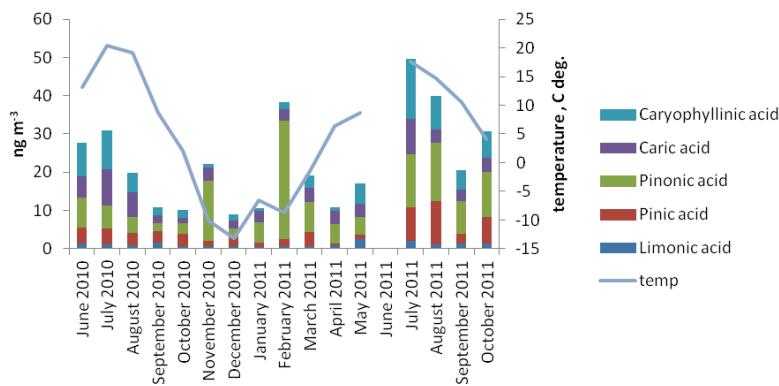


Fig. 2. Monthly means of terpenoic acid concentrations in PM_{2.5} fraction and mean temperature at a time of the measurements.

2878

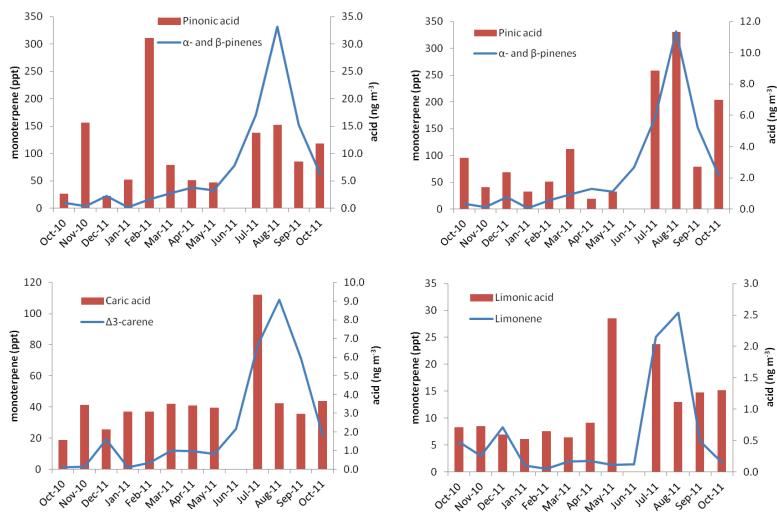


Fig. 3. Monthly mean terpenoic acid concentrations together with monthly mean monoterpene concentrations from Hakola et al. (2012).

2879

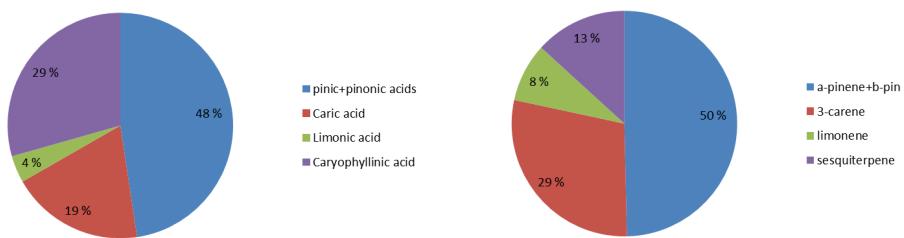


Fig. 4. Relative contributions of terpenoic acids in summer and average terpenoid emission fluxes from middle boreal forest in summer from Tarvainen et al. (2007).

2880

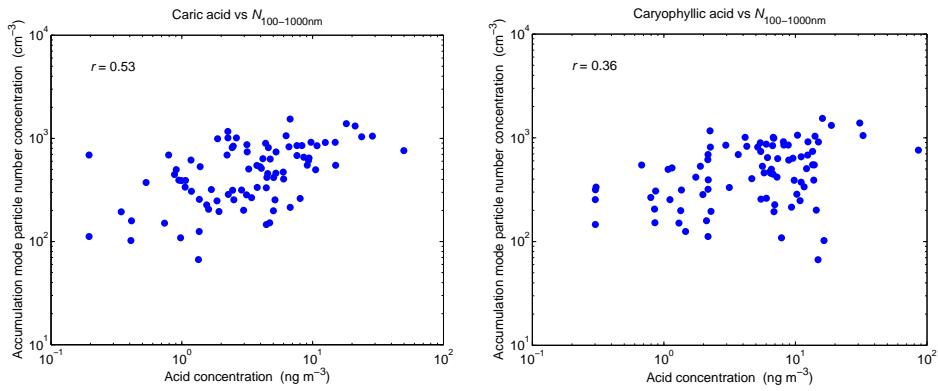


Fig. 5. Correlations between β -caryophyllinic and caric acids and the accumulation mode particle number concentrations.