Light-Dependent Monoterpene Emissions from an Oak Species Native to Asia

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This is the first report of light-dependent monoterpene emissions from an oak species native to Asia. Isoprenoids emitted by *Quercus phillyraeoides* were measured using branch enclosure methods. Sabinene, and α - and β -pinenes were the major compounds accounting for more than 90% of the total monoterpene emissions. The basal emission rates of total monoterpenes on leaf area and leaf dry weight bases ranged from 0.07 to 6.30 nmol m⁻² s⁻¹ and from 0.22 to 14.3 μ g g⁻¹ h⁻¹, respectively. A proton transfer reaction mass spectrometry measurement revealed that the emissions depend significantly on light intensity and leaf temperature. *Q. phillyraeoides* may be taxonomically close to European monoterpene-emitting oaks because it is morphologically close to the oaks native to the Mediterranean area, and because the geographical features of their habitats are similar to each other.

Keywords : emission model, monoterpene, light, Japanese evergreen oak, *Quercus phillyraeoides*, volatile organic compounds

INTRODUCTION

Biogenic volatile organic compounds (BVOCs) emitted by higher plants include terpenoids such as isoprene and monoterpenes, oxygenated low-molecular-weight compounds such as methanol, acetone, acetaldehyde, and ethanol, and a plant hormone ethylene. The estimation of annual global emission of all BVOCs has been conducted previously (e.g., Guenther et al., 1995; IPCC, 2001), according to which the estimated values greatly exceed the annual global emission of anthropogenic non-methane VOCs. Isoprene emission is the largest component and is estimated to comprise 50% of the annual global BVOC emission (Guenther et al., 1995).

Isoprene and monoterpenes are highly reactive VOC species and produce photochemical oxidants in a series of reactions with OH radical and NO. These reactions play an important role in influencing atmospheric chemistry related to regional photochemical oxidant formation (Fall, 1999) and lifetime of methane (Fehsenfeld et al., 1992). Recent studies have revealed that isoprene oxidation products may significantly contribute to the formation of secondary organic aerosols (Claeys et al., 2004).

Recently, indirect carbon emission resulting from BVOC emissions has been considered to be important. For example, Geron et al. (2002) roughly estimated that the BVOC emission offset is 10% or more of net ecosystem exchange of CO₂ (NEE) for a lowland tropical wet forest in Costa

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Rica. Guenther (2002) estimated that the annual global BVOC emission was 1.2 PgC.

Isoprene emission is related to light intensity and leaf temperature, but monoterpene emissions from plants with monoterpene-specific storage organs depend mainly on leaf temperature. Therefore, isoprene emission by plants can be described by leaf temperature and light intensity, and monoterpene emissions by leaf temperature, using simple algorithms developed by Guenther et al. (1993). In Europe and the United States, there have been various investigations to identify BVOC emitters and characterize their emissions. Trees in the genus *Quercus* have been recognized as strong isoprene emitters (Kesselmeier and Staudt, 1999). However, several Mediterranean oak species such as *Q. ilex* and *Q. coccifera* are reported to be monoterpene emitters, but have no storage organs (Kesselmeier et al., 1996). The monoterpene emissions of *Q. ilex* are strongly affected by light intensity and leaf temperature (Staudt and Seufert, 1995; Peñuelas and Llusà, 1999), and are successfully predicted by isoprene algorithms under steady state conditions (Ciccioli et al., 1997). On the other hand, the isoprenoid emissions by Asian plant species have been little studied (Yokouchi and Ambe, 1981; Klinger et al., 2002; Loreto et al., 2002; Tani et al., 2002). We have been conducting studies to identify isoprenoid emitters in Japan and investigate their emission characteristics (Tani and Fushimi, 2005; Okumura et al., 2008). *Quercus* trees occur widely in Japan and some of the deciduous species are strong isoprene emitters (Loreto, 2002; Tani and Kawawata, 2008). However, no *Quercus* monoterpene-emitters have so far been found in Japan or other countries in Asia. In our investigations, we have identified the native Japanese evergreen oak species, *Q. phillyraeoides*, as a monoterpene emitter. In this study, we show the monoterpene emission characteristics of *Q. phillyraeoides* as affected by leaf temperature and light intensity, and its basal emission rates.

MATERIALS AND METHODS

Plant materials

Four- to five-year-old saplings of *Q. phillyraeoides* were obtained from local nurseries in Yakushima Island, and Wakayama and Shizuoka Prefectures in Japan. The saplings were grown from seeds collected from each source habitat. There are large stands of *Q. phillyraeoides* in the three habitats. Five saplings of each habitat were prepared for the measurements. The plant heights ranged between 60 and 100 cm. Plants were potted in 20-L pots and placed in an experimental garden of Tokai University in Shizuoka, Japan, for at least one month, before being used for experiments. Branch enclosure measurements were conducted in a laboratory for all trees from September to November, 2006. Saplings derived from Wakayama Prefecture were also used for leaf cuvette measurements.

Branch enclosure method

To measure and identify isoprenoids emitted from leaves of *Q. phillyraeoides*, single branches of *Q. phillyraeoides* trees were enclosed in a transparent PFA bag (20 L). The PFA bag had an inlet and a sampling port at the side opposite the inlet. Outside air was pumped through a platinum catalyst system, with the temperature maintained at 400°C, to remove VOCs and other contaminants from the inflowing air. This purified air was then passed through a mass flow controller (SEC40, ESTEC, Japan) to keep the flow rate at 2.5 L min⁻¹ at the inlet of the enclosure bag. A 400-W metal halide lamp (D400, Toshiba LiTec, Japan) was fixed 2 m above the floor of the laboratory. The photosynthetic photon flux density (PPFD) ranged between 500–800 μmol m⁻² s⁻¹ at the top of the branch enclosed in the bag. The leaf temperature in the bag, monitored with two T-type fine thermocouples, ranged from 28 to 32°C in all the measurements. Two hours later, the inside air was collected into an adsorbent tube containing 200 mg Tenax TA and 100 mg Carbotrap B. The air was drawn into the adsorbent tubes from the sampling port by a pump (210 Pocket pump, SKC, USA) for 20 min at a flow rate of 130 μmol s⁻¹.

Leaf cuvette method

A portable photosynthetic measurement unit equipped with a controlled-environment broad leaf cuvette (LI6400, Li-Cor, USA) was used to investigate the effects of temperature and light intensity on isoprenoid emissions. For isoprenoid sampling, the outlet tube from the leaf cuvette was replaced by a Teflon tube. The outlet air flow was divided into two streams by a Teflon T-junction. One stream was reconnected to a built-in infrared gas analyzer (IRGA) in the cuvette and the other was used as a sampling port for isoprenoids. The inflow rate to the cuvette was $500 \mu\text{mol s}^{-1}$. The purified air, prepared by a platinum catalyst system, was supplied to the cuvette. The whole plant used for each measurement was placed under the metal halide lamp.

To examine the effects of light intensity on isoprenoid emissions, it was first set to $1,000 \mu\text{mol m}^{-2} \text{s}^{-1}$ and then decreased to 500, 200, 50, and $0 \mu\text{mol m}^{-2} \text{s}^{-1}$. Leaf temperature was kept at $25 \pm 0.2^\circ\text{C}$ in all the measurements. CO_2 concentration in the cuvette was kept at $380 \pm 10 \mu\text{L L}^{-1}$. To examine the effects of leaf temperature on isoprenoid emissions and physiological parameters, the leaf temperature was first set at 25°C and then raised to 30, 35, and 37.5°C . Light intensity was kept at $1,000 \pm 25 \mu\text{mol m}^{-2} \text{s}^{-1}$.

Isoprenoid concentrations in the cuvette were monitored with a proton transfer reaction mass spectrometer (PTR-MS) (Ionicon GmbH, Austria), and the data were obtained at ~ 1 -min intervals. The gas from the cuvette was successively collected in three adsorbent tubes after the isoprenoid emissions became stable for each PPFD and leaf temperature. The air was drawn into the adsorbent tubes from the sampling port by a pump (210 Pocket pump, SKC, USA) for 10 min at a flow rate of $130 \mu\text{mol s}^{-1}$. The PPFD and temperature changing experiments were conducted three times, each time using different leaves.

Isoprenoid analyses and data treatment

Isoprenoids collected in adsorbent tubes were identified and quantified with gas chromatography-mass spectrometry (GC-MS; QP5050A, Shimadzu, Japan). The samples underwent two-stage thermal desorption (Turbo Matrix ATD-40, Perkin-Elmer, USA) and compound separation was achieved using an SPB-5 capillary column ($60 \text{ m} \times 25 \text{ mm}$, $1 \mu\text{m}$ film thickness, Supelco, USA). GC analytical procedures and parameters are described in detail elsewhere (Tani et al., 2002). The emission rates were determined both on the leaf area and dry weight bases.

To determine if isoprenoids were accumulated in leaves of *Q. phillyraeoides*, discs (85 mm^2) were excised from the leaves at noon and isoprenoids in the leaf discs were extracted with 1 mL methanol. One- μL aliquots were analyzed with the GC-MS.

PTR-MS has been described in detail elsewhere (Lindinger et al., 1998; Hewitt et al., 2003). The drift tube E/N (where E is the electric field strength and N is the buffer gas number density in the drift tube) was kept at 130 Td by maintaining the drift tube voltage, temperature, and pressure at 520 V, 50°C , and 2.0 mbar, respectively. Standardized count per seconds (SCPS) of masses originating from isoprene and monoterpenes were calculated from PTR-MS signals minus the background signals and drift tube pressures (Tani et al., 2003). As large amounts of monoterpenes were detected with GC-MS analysis, total SPCS of masses 81 and 137 were considered. The total SPCS is not affected by humidity and therefore needs no correction for humidity (Tani et al., 2004). Since a linear regression for 4 to 5 data sets was observed between the total monoterpene concentration determined with GCMS and total SCPS of masses 81 and 137, the monoterpene concentration during the PTR-MS measurements was determined from the SCPS using the regression equation. Before conducting the measurements, the background SPCS of masses 81 + 137 in an empty cuvette was determined under different PPFD and temperature conditions, and these data were subtracted from the SPCS obtained during the emission measurements.

Isoprene emission model

Measured monoterpene emission rates for each PPFD and leaf temperature were normalized to basal emission rates under standard conditions of 30°C and $1,000 \mu\text{mol m}^{-2} \text{s}^{-1}$ PPFD using the

G93 isoprene algorithm (Guenther et al., 1993). The G93 algorithm describes the PPFD and temperature dependence of isoprene emissions as

$$M_m = M_s C_L C_T \quad (1)$$

where M_m is the isoprene emission rate at any temperature T (K), and light intensity L (PPFD, $\mu\text{mol m}^{-2} \text{s}^{-1}$) and M_s is the basal emission rate at a standard temperature T_s (303 K) and a standard PPFD ($1,000 \mu\text{mol m}^{-2} \text{s}^{-1}$). C_L and C_T are correction terms for light and temperature, respectively, defined as

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{1 + \alpha^2 L^2}} \quad (2)$$

$$C_T = \frac{\exp\{C_{T1}(T - T_s)/(RT_s T)\}}{1 + \exp\{C_{T2}(T - T_M)/(RT_s T)\}} \quad (3)$$

where R is the gas constant ($=8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and α ($=0.0027$ units), C_{L1} ($=1.066$ units), C_{T1} ($=95,000 \text{ J mol}^{-1}$), C_{T2} ($=230,000 \text{ J mol}^{-1}$), and T_M ($=314 \text{ K}$) are empirically derived constants.

RESULTS

Isoprenoid emission composition of Q. phillyraeoides

The emission composition of *Q. phillyraeoides* from three source habitats (Yakushima, Wakayama, and Shizuoka) is given in Fig. 1. The emissions in all the trees were dominated by sabinene ($34.5 \pm 5.2\%$), α -pinene ($39.4 \pm 3.8\%$), and β -pinene ($20.4 \pm 2.3\%$); their sum accounted for more than 90% of the total. The minor compounds were isoprene, α -thujene, camphene, myrcene, limonene, β -phellandrene, γ -terpinene, and linalool. No obvious difference of composition between source habitats was observed.

Monoterpene emission responses to light and leaf temperature

Figure 2 shows responses of total monoterpene emission rates (M_m) and net assimilation rate (A) of *Q. phillyraeoides* to light and leaf temperature. When PPFD was controlled at $1,000 \mu\text{mol m}^{-2} \text{s}^{-1}$, M_m and A increased gradually, and then reached a steady state (upper panel in Fig. 2). It took 2 h for M_m to become constant. When PPFD was changed to lower levels but leaf temperature was kept constant at 25°C , M_m started to decrease and reached a steady state within 20 min. This response of M_m to PPFD was similar to that of isoprene emission from isoprene emitters, and com-

Fig. 1 Emission composition of *Q. phillyraeoides* from three source habitats (Yakushima, Wakayama, and Shizuoka). Measurements were conducted at $500\text{--}800 \mu\text{mol m}^{-2} \text{s}^{-1}$ PPFD and $28\text{--}32^\circ\text{C}$ leaf temperature. The values on right side are the average emission rates on leaf area basis ($\text{nmol m}^{-2} \text{s}^{-1}$). Percentages of the monoterpene compositions are averages of five measurements using different saplings. Relative standard deviations of the percentages of sabinene and α - and β -pinenes are less than 10%.

pletely different from that of monoterpene emission from plants with storage organs. No detectable amounts of monoterpenes ($<0.3 \mu\text{g g}^{-1} \text{DW}$) were found in the leaf extracts from any of the three source habitats, suggesting that *Q. phillyraeoides* has no storage organs for monoterpenes.

In response to changing leaf temperature, M_m increased with an increase in leaf temperature (lower panel in Fig. 2). Maximum M_m was $3.51 \text{ nmol m}^{-2} \text{ s}^{-1}$ at 37.5°C leaf temperature, which was three times as much as M_m at 25°C . Monoterpene emission responses of the other two leaves were similar to this result.

Applying the isoprene algorithm for predicting monoterpene emission

The M_m values for each PPFD and leaf temperature shown in Fig. 2 were normalized to basal emission rates (M_s) under standard conditions of 30°C and $1,000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ PPFD using the G93 isoprene algorithm (Guenther et al., 1993). M_s values of the two leaves were determined as a slope of the regression line of M_m obtained under stable conditions against light factor (C_L) $\times$ leaf temperature factor (C_T). The M_m value was highly correlated with $C_L \times C_T$ in both the leaves ($r > 0.99$) and the calculated M_s values for upper and lower panels in Fig. 2 were 1.44 and $2.10 \text{ nmol m}^{-2} \text{ s}^{-1}$, respectively. To compare the measured M_m value with the estimated value (M_e), both the values are plotted together in Fig. 3. M_e values were in close agreement with the corresponding M_m values, suggesting that the G93 isoprene algorithm successfully estimates monoterpene emission from *Q. phillyraeoides*.

Basal emission rates of Q. phillyraeoides

Isoprenoid emission rates of the 15 trees measured using the branch enclosure method were

Fig. 2 Responses of total monoterpene emission rate and net assimilation rate (A) of *Q. phillyraeoides* to light and leaf temperature. Upper and lower panels show the responses to light intensity and leaf temperature, respectively. PPFD and leaf temperature varied from 0 to $1,000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ and from 25 to 37.5°C , respectively. The periods without monoterpene emission data were caused by adsorbent samplings for GC-MS analysis. The end of the Teflon tube exiting from the leaf cuvette was removed from the PTR-MS inlet and connected to the adsorbent tube. The samplings were initiated after the monoterpene emissions became stable.

normalized to M_s (Fig. 4). M_s on the leaf area basis in the three habitats (Yakushima, Wakayama, and Shizuoka) ranged between 0.07–3.10, 0.89–6.30, and 0.21–2.74 $\text{nmol m}^{-2} \text{s}^{-1}$, respectively. M_s on the leaf dry weight basis in the three habitats ranged between 0.22–6.56, 2.44–14.3, and 0.51–5.76 $\mu\text{g g}^{-1} \text{h}^{-1}$, respectively. As the tree-to-tree differences of emissions from identical source habitats were large, the M_s values were not significantly different between the three habitats.

DISCUSSION

Monoterpene emission and composition of Q. phillyraeoides

Loreto et al. (2002) reported that *Q. phillyraeoides* native to China did not emit a detectable amount of monoterpenes. On the other hand, we have detected certain amounts of monoterpene emissions from *Q. phillyraeoides* native to Japan. We used 15 saplings from three different habitats in Japan and confirmed that all of them emitted monoterpenes. Although the genetic variation between Chinese and Japanese *Q. phillyraeoides* may be a cause of this discrepancy, further research is required to clarify the detailed geographical variation of monoterpene emissions from *Q. phillyraeoides* grown in China, Japan, and other countries in East Asia.

Several Mediterranean evergreen oak species like *Q. ilex* and *Q. coccifera* are strong monoterpene emitters (BEMA, 1997; Kesselmeier et al., 1996). The major monoterpenes emitted

Fig. 3 Monoterpene emission rates measured in the experiments (M_m) and estimated using the isoprene algorithm of Guenther et al. (1993) (M_e). Basal emission rate (M_s) of each of the leaves was determined as a slope of the regression line of M_m against light factor (C_L) $\times$ leaf temperature factor (C_T).

Fig. 4 Basal emission rates of *Q. phillyraeoides* from three source habitats. Error bars represent maximum and minimum values.

by *Q. ilex* and *Q. coccifera* are α - and β -pinenes, sabinene, and myrcene. The minor compounds were α -thujene, ocimene, β -phellandrene, γ -terpinene, and linalool (e. g., Csiky and Seufert, 1999). Monoterpene emission and composition of *Q. phillyraeoides* are similar to those of *Q. ilex* and *Q. coccifera*. The monoterpene emissions of *Q. phillyraeoides* were strongly affected by light intensity and leaf temperature, as in the case of *Q. ilex*. On the other hand, M_s of *Q. phillyraeoides* was lower than those ($6\text{--}58\ \mu\text{g g}^{-1}\text{ h}^{-1}$) of *Q. ilex* and *Q. coccifera* (Kesselmeier and Staudt, 1999 and references therein). As the emission capacity might be significantly lower in potted saplings than in field-grown trees (Csiky and Seufert, 1999), it might also be the case with the M_s values obtained in our study.

Analogy between Q. phillyraeoides and Mediterranean monoterpene-emitting oak species

Q. phillyraeoides is a species for which the taxonomic classification is not entirely settled. For example, *Q. phillyraeoides* was classified into section *Cerris* based on morphological cladistic and chemo-taxonomic analyses (Manos et al., 1999). On the other hand, Flora of Japan (Iwatsuki et al., 2006) and Suzuki (1975) treated *Q. phillyraeoides* as subgenus *Sclerophyllodrys* and section *Ilex*, respectively.

Q. phillyraeoides is an evergreen oak species, and grows in poor soil, and dry and warm areas on the Pacific coast of Japan (Suzuki, 1975). Its leaf is smaller than those of any other Japanese *Quercus* spp. The acorn shell surface of *Q. phillyraeoides* is also squamate like the tree species classified in subgenus *Quercus*. Its habitat and morphologic features are very similar to those of the Mediterranean monoterpene-emitting oak species. Recent studies have suggested that the isoprenoid emissions by oak species are reliable taxonomical markers to distinguish subgenera or sections of *Quercus* (Loreto et al., 1998; Csiky and Seufert 1999; Loreto, 2002). Therefore, *Q. phillyraeoides* may be a species taxonomically close to European monoterpene-emitting oaks (e. g., *Q. ilex*).

CONCLUSION

We have identified the Japanese native evergreen oak species, *Q. phillyraeoides*, as a monoterpene emitter. Sabinene, and α - and β -pinenes were major compounds and accounted for more than 90% of the total monoterpene emissions. These emissions depend significantly on light intensity and leaf temperature. The G93 isoprene algorithm could successfully estimate monoterpene emission from *Q. phillyraeoides*. *Q. phillyraeoides* might be taxonomically close to European monoterpene-emitting oaks.

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