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# Development of a Compound-Specific Carbon Isotope Analysis Method for 2-Methyltetrols, Biomarkers for Secondary Organic Aerosols from Atmospheric Isoprene

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**The stable carbon isotope compositions of 2-methyltetrols, biomarker compounds for secondary organic aerosols formed from isoprene in the atmosphere, have been determined by gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS). In this work, isoprene with various $\delta^{13}C$ values was used to produce 2-methyltetrols via an oxidation reaction with hydrogen peroxide in sulfuric acid under direct sunlight. The target compounds with different stable carbon isotope compositions were then derivatized by methylboronic acid with a known $\delta^{13}C$ value and measured by GC/C/IRMS. With $\delta^{13}C$ values of 2-methyltetrols and methylboronic acid predetermined, isotopic fractionation is evaluated for the derivatization process. Through reduplicate $\delta^{13}C$ measurements, the carbon isotope analysis achieved excellent reproducibility and high accuracy with an average error of <0.3‰. The differences between the predicted and measured $\delta^{13}C$ values range from −0.10 to 0.29‰, indicating that the derivatization process does not introduce isotopic fractionation. The $\delta^{13}C$ values of 2-methyltetrols could be calculated on the basis of the stoichiometric mass balance equation among 2-methyltetrols, methylboronic acid, and methylboronate derivatives. Preliminary tests of 2-methyltetrols in $PM_{2.5}$ aerosols at two forested sites were conducted and revealed significant differences in their isotope compositions, implying possible application of the method in helping us understand the primary emission, photochemical reaction, or removal processes of isoprene in the atmosphere.**

Evidence that isoprene contributes to the formation of secondary organic aerosols (SOAs) has been obtained from both field and chamber experiments.[1−6] It was demonstrated that isoprene and its gas-phase oxidation products, methacrolein (MACR) and methyl vinyl ketone (MVK), could be converted in aqueous solution into 2-methyltetrols, i.e., 2-methylerythritol and 2-methylthreitol, through an acid-catalyzed reaction with hydrogen peroxide, which is formed in the atmosphere via recombination of hydroperoxy radicals.[2] Recent laboratory studies of isoprene photooxidation showed SOA formation at precursor concentrations as low as 10 ppb. The aerosol yield of isoprene from a laboratory study is in the range of 1−5%.[7] However, there are significant uncertainties with respect to the true impact of atmospheric aerosols on climate and health because of a lack of knowledge of their sources, composition, properties, and mechanisms of formation.[8]

Isotopic composition measurements have been extremely useful for improving our understanding of the sources, sinks, and distribution of atmospheric trace gases. It has been shown that changes in the stable carbon isotope ratios can be used as

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indicators of atmospheric processing of volatile organic compounds;[9] for example, carbon isotope ratio measurements allow the calculation of the extent of photochemical processing of isoprene in the atmosphere.[10] Furthermore, Rudolph et al.[11] developed a gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) technique to measure the stable carbon isotope ratios of isoprene and its gas-phase oxidation products, MACR and MVK, and to gain insight into the atmospheric oxidation of isoprene. Very recently, this group has reported studies on the stable carbon kinetic isotope effects (KIE) of the reactions of isoprene, MACR, and MVK with OH radicals, as well as with ozone in the gas phase.[12−14] These data are valuable for obtaining insight into the role of loss processes in determining the atmospheric mixing ratios. However, there are no isotopic studies of isoprene SOA products in the aerosol phase.

Methylboronic acid (MBA) has been reported to determine natural $^{13}$C abundances of monosaccharides by derivatizing adjacent hydroxyl groups of monosaccharides followed by *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) derivatization of the remaining single OH groups.[15,16] Recently, Boschker et al.[17] reported a versatile method for stable carbon isotope analysis of carbohydrates by high-performance liquid chromatography/isotope ratio mass spectrometry. To develop a compound-specific isotope analysis method for 2-methyltetrols, marker compounds of photooxidation products of isoprene, a technique from our previous work was adapted.[18] MBA was used as the derivatization reagent prior to gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS). The derivatizing C from the reagent accounts for 29% of the analyte in the boronates, but 70% in the trimethylsilyl (TMS) derivatives. Therefore, the sensitivity of the MBA method should be high. The oxidation reaction of isoprene, atmospheric sampling, accuracy, and reproducibility of the method will be discussed in detail, and the stable carbon isotope effects during the procedure will be evaluated. $\delta^{13}$C data for atmospheric 2-methyltetrols will also be presented to demonstrate the practical utility of this method.

## EXPERIMENTAL SECTION

**Materials.** Isoprene was obtained from three suppliers: Fluka, Sigma-Aldrich (>98% pure, **M1**); Alfa-Aesar (Lancaster, England) (99% pure, **M2**); and Toyo Kasei Kogyo Co. (Osaka, Japan) (99% pure, **M3**). Hydrogen peroxide (30% in water) was purchased from Guoyao (Shanghai, China). Methylboronic acid (MBA) was purchased from ABCR GmbH and Co. KG (Karlsruhe, Germany) (97% pure) and recrystallized three times from a benzene/acetone mixture (3:1). MBA of the same lot number was used for all derivatizations. Anhydrous pyridine (99% pure) was supplied by Acros Organics (Geel, Belgium). BSTFA [*N*,*O*-bis(trimethylsilyl) trifluoroacetamide] was purchased from Pierce (Rockford, IL). All solvents employed were HPLC grade.

**Preparation of Standard 2-Methyltetrols.** 2-Methyltetrols were made by photooxidation of isoprene, which we conducted by exposing a 30 mL flask with a mixture of 5 mL of 30% $H_2O_2$ and 5 mL of isoprene (0.05 mol, 3.4 g) to sunlight. A few drops of sulfuric acid (0.1 M) was added until the pH of reaction mixture was between 1 and 2. The resulting mixture was then maintained with continuous and vigorous stirring in sunlight for 4 h;[19] 15 mg of barium carbonate was added to 1 mL of the reacted solution for neutralization. After centrifugation, the supernatant was dried, and a slightly yellow oil (2.5 g, 36% yield) was obtained. It worth noting that exposure to sunlight is crucial for the production of 2-methyltetrols.

The purification of crude 2-methyltetrols was performed according to a procedure reported by Wang et al.[20] The purity of 2-methyltetrols was verified by gas chromatography/mass spectrometry (GC/MS) after they had been derivatized with BSTFA, and the $\delta^{13}$C value was determined by elemental analyzer/isotope ratio mass spectrometry (EA/IRMS).

**Derivatization of 2-Methyltetrols.** The derivatization technique of 2-methyltetrols with methylboronic acid was adapted from Wang et al.;[18] 100 $\mu$L of a solution of 2-methyltetrols (approximately 1 mg/mL in methanol) was dried under a gentle nitrogen flow, and then 5 mL of a solution of 1 mg of methylboronic acid in 10 mL of anhydrous pyridine was added. The molar ratio of MBA to 2-methyltetrols was ~10:1. The mixture was allowed to react at 60 °C for 60 min. It should be noted that the pretreatment of pyridine with 4 Å molecular sieves in excess is crucial for a successful MBA derivatization. The $\delta^{13}$C value of methylboronic derivatives was determined by gas chromatography/combustion/isotopic ratio mass spectrometry (GC/C/IRMS).

**Measurements of the $\delta^{13}$C Value of Standard Isoprene.** The method for determining the $\delta^{13}$C value of isoprene was as follows.[21] Isoprene (1 mL) was sealed in a 2 mL glass vial with an open screw cap containing a Teflon-lined silica septum. After ~1 h for equilibrium, 15 $\mu$L gas samples from the glass bottle were injected into the split/splitless injection port of the gas chromatograph using a Hamilton gastight locking syringe.

**Aerosol Sampling.** Samples were collected in boreal-temperate Changbai Mountain Forest Ecosystem Research Station in Jilin Province and subtropical Dinghu Mountain Nature Reserve in Guangdong Province. The details for sampling sites have been described previously.[6] The sampling occurred during the summer when the meteorological conditions and the maximum solar radiation, as well as high temperatures, were favorable for the photooxidation of isoprene. A high-volume $PM_{2.5}$ air sampler

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(Graseby-Andersen) was operated at a flow rate of 1.13 $m^3$/min, and Whatman quartz fiber filters (20.3 cm × 25.4 cm) were used; 24 h samplers were collected. All filters were baked at 550 °C for 4 h to remove organic contaminants. After collection, the filters were stored at −20 °C until they were analyzed. Part of the filters was extracted with methanol. The solvent was then concentrated, filtered, and finally dried completely. All samples were derivatized using the same procedure as described above and measured by GC/C/IRMS.

**Analytical Systems.** The gas chromatography/mass spectrometry (GC/MS) instrument consisted of a Hewlett-Packard (Fullerton, CA) model 6890 gas chromatograph equipped with a DP-5MS device (30 m × 0.25 mm inside diameter, 0.25 $\mu$m film thickness), coupled to a Hewlett-Packard model 5975MSD quadrupole analyzer. Data were acquired and processed with ChemStation (Hewlett-Packard). The temperature program was as follows: initial temperature at 100 °C held for 5 min, a gradient of 3 °C/min up to 200 °C, a gradient of 30 °C/min up to 290 °C, held for 2 min. The mass spectrometer was operated in the electron ionization mode at 70 eV and an ion source temperature of 150 °C. Full scan mode was used in the mass range of *m/z* 50−420.

Two kinds of gas chromatography/combustion/isotopic ratio mass spectrometry (GC/C/IRMS) systems were used in this study. The analysis of MBA derivatives was performed on an HP 6890 GC system (Agilent, Santa Clara, CA) equipped with a DP-5MS device (30 m × 0.25 mm × 0.25 $\mu$m), connected to an isotope ratio mass spectrometer (Isoprime, GV instrument, Manchester, U.K.). The oven temperature program was as follows: initially at 60 °C, a gradient of 4 °C/min up to 110 °C, held for 2 min, a gradient of 50 °C/min up to 290 °C, held for 2 min. The injector was set at 250 °C in splitless mode. Helium was used as the carrier gas at 1.5 mL/min. $CO_2$ with a known $\delta^{13}C$ value (−26.65‰) was used as the external reference gas. The combustion furnace containing the CuO catalyst and the reduction oven containing the Cu catalyst were kept at 940 and 650 °C, respectively. The temperature of the interface between the GC and combustion furnace was set at 290 °C. The reproducibility and accuracy of carbon isotopic analyses were evaluated routinely every day using 10 laboratory isotopic standards ($C_{12}$, $C_{14}$, $C_{16}$, $C_{18}$, $C_{20}$, $C_{22}$, $C_{25}$, $C_{28}$, $C_{30}$, and $C_{32}$ *n*-alkanes supplied by Indiana University, Bloomington, IN) with known isotopic values (−31.89, −30.67, −30.53, −31.02, −32.24, −32.77, −28.49, −32.11, −33.05, and −29.41‰, respectively). 2-Methyltetrol methylboronates prepared in the laboratory were analyzed 10 times and used as laboratory standards. For $\delta^{13}C$ analysis of isoprene, the same GC/C/IRMS system described above and a CP-PoraPLOT Q column (25 m × 0.32 mm × 10 $\mu$m, Varian) were used. The GC was run in a split ratio of ∼40:1, and the injector was set at 150 °C. The initial oven temperature was held at 120 °C for 1 min, followed by a gradient of 20 °C/min up to 195 °C, at which point the temperature was held for 10 min. Standard $CO_2$ ($\delta^{13}C$ = −26.65‰) was used as the external reference gas. $CH_4$ with a known $\delta^{13}C$ value (−36.30‰) was used as the laboratory isotopic standard to check the reproducibility and accuracy of the carbon isotopic analysis routinely.[22] For both analysis systems, the sextuple analysis of laboratory isotopic standards indicated excellent accuracy and reproducibility of carbon isotopic analysis [the corresponding standard deviation ranged from 0.13 to 0.30‰, and the deviation between the measured data and the predetermined data ranged from −0.02 to 0.13‰ (Table 1S of the Supporting Information)].

Elemental analyzer/isotope ratio mass spectrometry (EA/IRMS) was performed as follows. Standard 2-methyltetrols and recrystallized methylboronic acid were put into cleaned tin capsules and weighed, repectively. Capsules containing weighed samples were placed in the CE (Wigan, U.K.) EA1112 C/N/S analyzer and burned at 960 °C in an $O_2$ atmosphere in a combustion tube. Combustion gases were swept through a reduction oven and entered a GC column where $CO_2$ was separated from other gases. Then the $CO_2$ passed through a Conflo III interface (Finnigan, Waltham, MA) and entered a $\mathrm{DELTA}^{\mathrm{plus}}$ XL mass spectrometer (Thermo Finnigan MAT, Bremen, Germany) where it was compared to the reference $CO_2$ with a known $\delta^{13}C$ value (−29.10‰, calibrated against the NBS-22 reference material with a $\delta^{13}C$ value of −29.70‰). During every batch of analyses, an empty tin capsule was analyzed as a blank to check the background, and the carbon black sample with a known $\delta^{13}C$ value (−36.91‰) was used to evaluate the reproducibility and accuracy. The standard deviation of analysis and the deviation between the measured data and the predetermined data were less than 0.3‰ (Table 2S of the Supporting Information).

All $^{13}C$:$^{12}C$ ratios are expressed in conventional delta ($\delta$) notation, which is the per mil (‰) deviation from the standard Vienna Pee Dee Belemnite (VPDB) reference point.

## RESULTS AND DISCUSSION

**$\delta^{13}C$ Analysis of Standard 2-Methyltetrols.** Figure 1 shows a typical total ion current (TIC) GC/MS chromatogram from isoprene oxidation products derivatized by BSTFA. Identification of these two major compounds was made by comparison of the retention time and mass spectra with those published in the literature.[1,6,20] Figure 2 presents the TIC GC/MS chromatogram of 2-methyltetrol−MBA derivatives. The mass spectra of these three compounds are very similar, as could be expected for diastereoisomers. The mass spectrum of compound **2** reveals a tiny molecular ion (*m/z* 184). Characteristic ions at *m/z* 99 and 85 correspond to the cleavage of the C−C bond at the $C_2$ position. Other ions at *m/z* 69, 57, and 43 can be explained by the further fragment of the ion at *m/z* 85 or 99.

The $\delta^{13}C$ values of methylboronic acid and standard 2-methyltetrols were determined by EA/IRMS to be −24.96 ± 0.06‰ (eight measurements) and −32.40 ± 0.14‰ (*n* = 6, from **M1**), −29.84 ± 0.12‰ (*n* = 6, from **M2**), and −32.36 ± 0.18‰ (*n* = 6, from **M3**) (Table 1).

**$\delta^{13}C$ Analysis of MBA Derivatives.** In derivatization, the preparation of 2-methyltetrol−MBA derivatives alters the original stable isotope compositions of the 2-methyltetrols. To correct for the introduction of carbon during derivatization, it is necessary to assess the isotopic reproducibility of the derivatization method.

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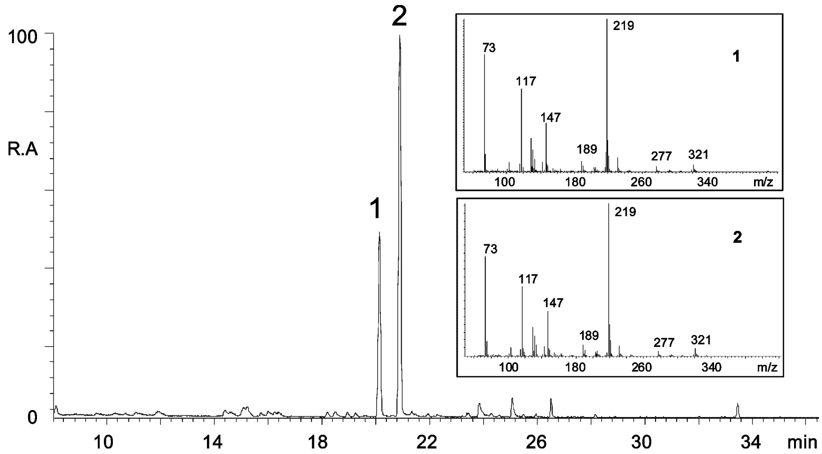

**Figure 1.** GC/MS total ion chromatograms obtained for the reaction mixtures of isoprene with $H_2O_2$ and sulfuric acid derivatized by BSTFA and spectra for products (insets) **1** (2-methylthreitol) and **2** (2-methylerythritol).

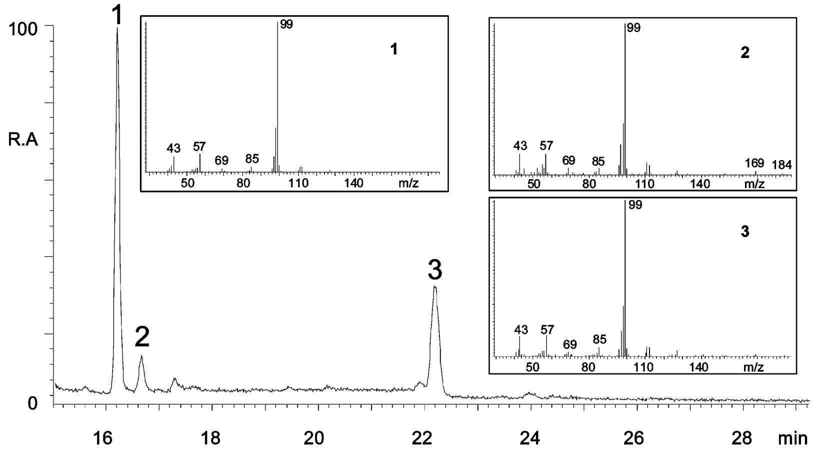

**Figure 2.** GC/MS total ion chromatogram obtained for 2-methyltetrols derivatized by MBA and mass spectra for the products (insets). Compounds **1** and **2** correspond to 2-methylerythritol−MBA derivatives, and compound **3** corresponds to a 2-methylthreitol−MBA derivative.

**Table 1. Stable Carbon Isotopic Compositions of Isoprene, 2-Methyltetrols (2-MT), and MBA Derivatives Measured and Predicted in the Derivatization Reaction**

| | $\delta^{13}C^{a}$ | | | | |
|---|---|---|---|---|---|
| supplier | measured isoprene[b,c] | measured 2-MT[b,d] | measured methylboronates[b,c,e] | calculated methylboronates[b,f] | $\Delta^{g}$ |
| **M1** | −24.54 ± 0.18 ($n = 7$) | −32.40 ± 0.14 ($n = 6$) | −29.98 ± 0.22 ($n = 6$) | −30.27 | 0.29 |
| **M2** | −23.72 ± 0.23 ($n = 7$) | −29.84 ± 0.12 ($n = 6$) | −28.08 ± 0.15 ($n = 6$) | −28.24 | 0.16 |
| **M3** | −25.19 ± 0.19 ($n = 7$) | −32.36 ± 0.18 ($n = 6$) | −30.35 ± 0.16 ($n = 6$) | −30.25 | −0.10 |

[a] Stable carbon isotopic compositions reported in per mil relative to PDB. [b] Arithmetic means and standard deviations. [c] $\delta^{13}C$ values determined by GC/C/IRMS. [d] $\delta^{13}C$ values determined by EA/IRMS. [e] Derivatized by methylboronic acid with a $\delta^{13}C$ value of −24.96 ± 0.06‰ (eight measurements) determined by EA/IRMS. [f] On the basis of mass balance relationship eq 1. [g] Calculated $\delta^{13}C$ − measured $\delta^{13}C$.

The reproducibility of the carbon isotope composition for three 2-methyltetrols (with different $\delta^{13}C$ values) was evaluated. Their $\delta^{13}C$ values and those of the corresponding MBA derivatives are listed in Table 1. The analytical errors (standard deviation) obtained for six EA/IRMS analyses of 2-methyltetrols produced from isoprene from the same supplier ranged from 0.12 to 0.18‰, with an average of 0.15 ± 0.03‰, while for GC/C/IRMS analyses of MBA derivatives, the analytical errors were from 0.15 to 0.22‰, with an average of 0.17 ± 0.04‰. The reproducibility compares well with those obtained in the derivatization of fatty acids.[23]

**Isotopic Effects of the Method.** According to eq 1, the theoretical $\delta^{13}C$ values of methylboronates can be calculated according to stoichiometric mass balance and reflect the relative contributions of carbon from 2-methyltetrols, methylboronic acid, and their respective $\delta^{13}C$ values:

$$\delta^{13}C_{\text{methylboronate}} = f_{\text{MBA}}\delta^{13}C_{\text{MBA}} + f_{\text{2-methyltetrol}}\delta^{13}C_{\text{2-methyltetrols}} \tag{1}$$

where $f_{\text{MBA}}$ and $f_{\text{2-methyltetrol}}$ are the molar fractions of carbon in methylboronate arising from underivatized 2-methyltetrol and MBA reagent, respectively. Here, $f_{\text{MBA}} = {}^{2}/_{7}$, and $f_{\text{2-methyltetrols}} = {}^{5}/_{7}$. The stable carbon isotopic compositions obtained for 2-methyltetrols and derivatives are listed in Table 1. The measured data for methylboronates were compared with

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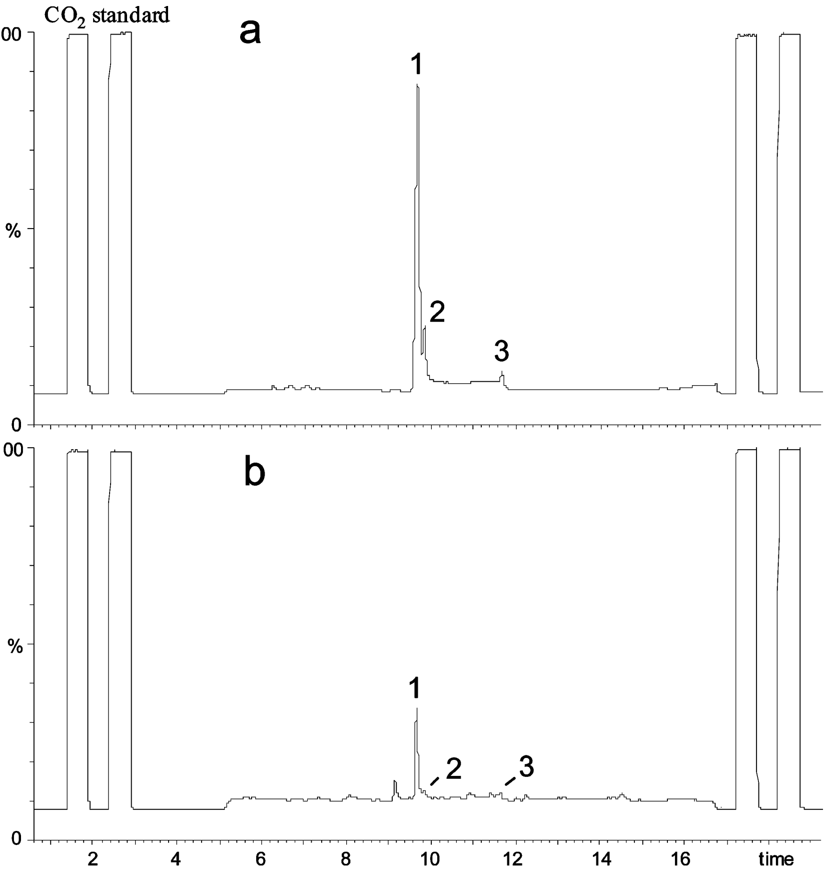

**Figure 3.** GC/C/IRMS chromatogram of 2-methyltetrol−MBA derivatives: (a) standard derivative and (b) extract of the fine size fraction of a 24 h Hi-Vol aerosol sample collected at Dinghu, China, on August 2, 2006. Compounds **1** and **2** are 2-methylerythritol−MBA derivatives, and compound **3** is the 2-methylthreitol−MBA derivative.

those predicted by eq 1. The predicted and measured $\delta^{13}$C values of methylboronates agreed well with each other.

According to Rieley's discussion of the kinetic isotope effect,[24] when a bond containing the carbon atom under consideration is changed in the rate-determining step, the primary isotopic effect is the most significant. If no carbon bond changed in the rate-determining reaction or if no carbon-containing bond is involved in this step, there should not be a primary isotope effect on the $\delta^{13}$C value. In this work, four hydroxyl groups from two molecules of MBA react with four hydroxyl groups of 2-methyltetrol and eliminate four molecules of water. No other carbon-containing bonds, except C−O bonds of 2-methyltetrols, are involved in the reaction. The difference between measured and calculated $\delta^{13}$C values of methylboronic derivatives ranged from −0.10 to 0.29‰ (Table 1). Accuracy was well within the isotope technical specification (±0.5‰). It should be pointed out that the analytical error of the calculated data for underivatized 2-methyltetrol (usually expressed as the standard deviation, *S*) could be calculated by the following equation:

$$S_{\text{2-methyltetrol}}{}^2 = (1/f_{\text{2-methyltetrol}})^2 S_{\text{methylboronate}}{}^2 + (f_{\text{MBA}}/f_{\text{2-methyltetrol}})^2 S_{\text{MBA}}{}^2 \qquad (2)$$

where $f_{\text{MBA}}$ and $f_{\text{2-methyltetrol}}$ are the same as in eq 1 and $S_{\text{2-methyltetrol}}$, $S_{\text{MBA}}$, and $S_{\text{methylboronate}}$ are the analytical standard deviations of 2-methyltetrols, MBA, and methylboronates, respectively. In this work, $S_{\text{MBA}}$ was 0.06‰ and $S_{\text{methylboronate}}$ was 0.17 ± 0.04‰ (0.15−0.22‰). According to eq 2, the standard deviation of the measured $\delta^{13}$C value of 2-methyltetrol ranged from 0.21 to 0.31‰. The results imply that the method is promising and introduces no isotopic fractionation in the derivatization process, as confirmed by Table 1. The stable carbon isotopic determination exhibited high precision and good reproducibility.

On the other hand, precursor isoprene was approximately 6.12−7.86‰ more enriched in $^{13}$C than 2-methyltetrols (Table 1). This might reflect isotope fractionation during the photochemical oxidation reaction. Rudolph et al.[12] reported that the stable carbon isotope fractionation for the reaction of isoprene with OH radicals in the gas phase was 6.94 ± 0.80‰, very similar to the value in this work.

To fully evaluate the usefulness of relating precursor isoprene $\delta^{13}$C values to those measured in aerosol, one must investigate the potential for the primary kinetic isotope effect (KIE) involving the carbon−carbon bond cleavage products (such as methylglyceric acid, glyoxal, and methylglyoxal) to influence the $\delta^{13}$C value of 2-methyltetrols. This is especially true since the reaction pathways for formation of 2-methyltetrols remain unclear. Gas-phase and mixed-phase mechanisms involving the aqueous aerosol phase have been considered.[1−3]

**Measurements of Atmospheric Samples.** The target compounds in samples were well-separated (Figure 3), while the 2-methylerythritol derivative gave rise to double peaks, due to the

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**Table 2. Concentrations and Stable Carbon Isotopic Compositions of 2-Methyltetrols at Two Forested Sites**

| | | | $\delta^{13}C^a$ | |
|---|---|---|---|---|
| sampling site | sampling date | concentration of 2-methyltetrols (ng/m$^3$) | measured methylboronates$^b$ | calculated 2-MT$^c$ |
| Changbai | July 27, 2007 | 76.29 | $-24.27 \pm 0.13$ ($n = 3$) | $-24.00 \pm 0.18$ |
| | July 28, 2007 | 108.8 | $-24.79 \pm 0.61$ ($n = 3$) | $-24.73 \pm 0.86$ |
| Dinghu | August 1, 2006 | 65.30 | $-27.29 \pm 0.10$ ($n = 3$) | $-28.22 \pm 0.14$ |
| | August 2, 2006 | 83.54 | $-26.93 \pm 0.46$ ($n = 3$) | $-26.99 \pm 0.64$ |

[a] Stable carbon isotopic compositions reported in per mil relative to PDB. [b] Arithmetic means and standard deviations. Derivatized by methylboronic acid with a $\delta^{13}C$ value of $-24.96 \pm 0.06$‰ (eight measurements) determined by EA/IRMS. $\delta^{13}C$ values determined by GC/C/IRMS. [c] Arithmetic means of calculated $\delta^{13}C$ values based on mass balance relationship eq 1 and standard deviations (*S*) calculated according to eq 2.

formation of both *E* and *Z* isomers during the reaction. From our previous work,[18] the erythro form of tetrols, erythritol, eluted earlier than the threo form, threitol. Under the same conditions, peaks 1 and 2 were identified as (*Z*)- and (*E*)-2-methylerythritol−MBA derivatives, respectively, while peak 3 was the 2-methylthreitol−MBA derivative. The latter derivative gives rise to only one tiny peak, due to the stereo hindrance of the 2-methyl group. The $\delta^{13}C$ value of the 2-methyltetrol−MBA derivatives was obtained by defining these three peaks as one using the integral tools of IRMS.

It could be seen from Table 2 that $\delta^{13}C$ values of 2-methyltetrols were distinctly different for the two sites. It has been documented that there were significant differences in carbon isotope ratios among C3, C4, and CAM plants, e.g., −35 to −23‰ for C3 with an average of −26‰, −14 to −10‰ for C4 with an average of −13‰, and intermediate carbon isotope compositions for CAM.[25] The $\delta^{13}C$ of 2-methyltetrols might reveal the relation of atmospheric aerosol with the vegetation types and be used as an indicator of proportions of C3 to C4 plants in vegetation.

## CONCLUSIONS

The stable carbon isotope compositions of 2-methyltetrols, biomarker compounds of isoprene in atmospheric aerosols, were determined by GC/C/IRMS. MBA was used as the derivatization reagent which allows only 29% contribution of the analyzed C. The $\delta^{13}C$ values of 2-methyltetrols are calculated on the basis of the stoichiometric mass balance equation among 2-methyltetrols, methylboronic acid, and methylboronate derivatives. Excellent reproducibility and accuracy are achieved without carbon isotopic fractionation. Moreover, photosynthesis of 2-methyltetrols through photochemical oxidation of isoprene is introduced. The $\delta^{13}C$ values of atmospheric 2-methyltetrols were determined for two forest aerosols. Considering the complex formation pathways of 2-methyltetrols, this technique will be helpful for full field application and will have potential in differentiation between homogeneous and heterogeneous oxidation processes. The application of this method may provide additional information about the sources and sinks of atmospheric isoprene. Further experiments on photochemical oxidation in a smog chamber are warranted.

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## SUPPORTING INFORMATION AVAILABLE

$\delta^{13}C$ values (‰) of the Indiana reference *n*-alkanes measured by GC/C/IRMS (Isoprime) (Table 1S) and $\delta^{13}C$ values of the reference materials of $CH_4$ and carbon black (Table 2S). This material is available free of charge via the Internet at http://pubs.acs.org.

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