Characterization and Quantification of Isoprene-Derived Epoxidiols in Ambient Aerosol in the Southeastern United States


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Isoprene-derived epoxidiols (IEPOX) are identified in ambient aerosol samples for the first time, together with other previously identified isoprene tracers (i.e., 2-methyltetrols, 2-methylglyceric acid, C5-alkenetriols, and organosulfate derivatives of 2-methyltetrols). Fine ambient aerosol collected in downtown Atlanta, GA and rural Yorkville, GA during the 2008 AMIGAS campaign was analyzed using both gas chromatography/quadrupole mass spectrometry (GC/MS) and gas chromatography/time-of-flight mass spectrometry (GC/TOFMS) with prior trimethylsilylation. Mass concentrations of IEPOX ranged from ~1 to 24 ng m⁻³ in the aerosol collected from the two sites. Detection of particle-phase IEPOX in the AMIGAS samples supports recent laboratory results that gas-phase IEPOX produced from the photooxidation of isoprene under low-NOₓ conditions is a key precursor of ambient isoprene secondary organic aerosol (SOA) formation. On average, the sum of the mass concentrations of IEPOX and the measured isoprene SOA tracers accounted for about 3% of the organic carbon, demonstrating the significance of isoprene oxidation to the formation of ambient aerosol in this region.

Introduction

Isoprene (2-methyl-1,3-butadiene, C₅H₈) is the most abundant nonmethane hydrocarbon emitted into the Earth’s atmosphere, with a global source estimated to be 440–660 Tg C year⁻¹ (1). Recent field, experimental, and modeling studies have shown that SOA formation from isoprene oxidation contributes significantly to the ambient organic aerosol budget, affects regional air quality, and impacts global climate (ref 2 and references therein).

Recently, Paulot et al. (3) reported that gas-phase IEPOX is produced in high yields from the OH-initiated oxidation of isoprene under low-NOₓ conditions. Calculations from a chemical transport model, GEOS-Chem, indicated that the mixing ratios of IEPOX in the planetary boundary layer (PBL) over the southeastern United States could reach values as high as 0.5 ppb during the summer, which is consistent with levels observed in preliminary airborne measurements (3). Reactive uptake of gas-phase IEPOX onto acidified sulfate seed aerosol, demonstrated in laboratory chamber studies, revealed that these compounds are likely a key gas-phase intermediate responsible for the formation of isoprene low-NOₓ SOA (4). Acid-catalyzed ring-opening reactions of epoxides in the particle phase are kinetically favorable under typical tropospheric conditions (5), leading to the formation of known isoprene SOA tracers (e.g., 2-methyltetrols and their corresponding organosulfates) (4). These compounds have been identified in ambient aerosol (ref 6 and references therein). Overall, recent results from laboratory and modeling studies have shown that IEPOX is likely an important precursor to the formation of isoprene SOA.

In the present work, fine ambient aerosol samples were collected in downtown Atlanta, GA and a rural location in Yorkville, GA during the 2008 AMIGAS campaign. The AMIGAS campaign was conducted in order to increase understanding of the interactions between biogenic and anthropogenic emissions; specifically, this campaign was designed to address the following questions: (I) How do atmospheric reactions between biogenic and anthropogenic emissions impact the formation of SOA? (II) What are the mechanisms regulating the chemistry of primary organic aerosol (POA) and SOA, and how do these processes differ between day and night? (III) Which compounds contribute to the atmospheric nitrogen loading, and how do these ambient nitrogen compounds impact atmospheric chemistry and ensuing air quality?

Although the present manuscript does not explicitly address all of the goals (or questions) of the AMIGAS campaign outlined above, especially those related to POA, we chemically characterize and quantify, for the first time, particle-phase IEPOX in ambient aerosol.

In addition to quantifying the aerosol mass concentrations for IEPOX, we also quantify other known isoprene SOA tracers, which include the 2-methyltetrols, C₅-alkenetriols, 2-methylglyceric acid, as well as the organosulfates of the 2-methyltetrols (i.e., hydroxy sulfate esters), to evaluate the correlation between these SOA tracers and gain insight into their potential formation pathways in the atmosphere. It is noted that the detection of particle-phase IEPOX and its known reaction products (i.e., the 2-methyltetrols, organosulfates of the 2-methyltetrols) in ambient aerosol provides
direct evidence for the chemical interaction of biogenic emissions and anthropogenic pollutants (i.e., SO$_2$) leading to the formation of isoprene SOA. The latter provides direct insights into questions (I) and (II) outlined above for the AMIGAS campaign, especially those related to SOA formation in this region. Additionally, the detection of IEPOX and its known heterogeneous-reaction products is consistent with recent remote sensing data over the southeastern United States that show biogenic volatile organic compounds combine with anthropogenic pollutants to form substantial amounts of SOA (7).

**Experimental Section**

The Southeastern Aerosol Research and Characterization (SEARCH) network served as the operating platform for the 2008 AMIGAS campaign. SEARCH was chosen due to its location in a region experiencing significant biogenic and anthropogenic emissions, and in which an extensive high-quality long-term data set is available (8-10). Detailed descriptions of the sampling sites, aerosol sampling, and particle-phase measurements are given by Hansen et al. (8) and Edgerton et al. (9-11). Additional instrumentation from numerous research laboratories across the United States were installed for AMIGAS at the urban Atlanta, GA (at Jefferson Street (JST)), and rural Yorkville, GA (YRK), sites, which complemented the ongoing SEARCH measurements at these locations. The AMIGAS campaign was conducted from August 1 to September 15, 2008. Day (10 a.m. to 6 p.m., local time) and night (10 p.m. to 6 a.m., local time) segregated PM$_{2.5}$ (particulate matter with an aerodynamic diameter <2.5 μm) high-volume quartz filter samples (i.e., quartz microfibre, 20.3 x 25.4 cm, Whatman) were collected daily from both the JST and YRK sites from August 1 through September 10, 2008, which provided significant overlap with other chemical measurements made at each site. A select number of filters (14 from JST and 6 from YRK) were chemically characterized for the present study; these filters were primarily selected based on the high aerosol loadings and carbon-to-sulfur ratio observed during their respective sampling periods. Averaged gas-phase concentrations of O$_3$, CO, SO$_2$, and NO$_x$ during the sampling period are given in Supporting Information (SI) Table S1.

Isoprene SOA was generated from the photooxidation of isoprene under low-NO$_x$ conditions in the presence of acidified sulfate seed aerosol in the Caltech dual indoor 28 m$^3$ Teflon smog chambers. Details of the experimental protocols have been outlined previously by Suratt et al. (4). Isoprene SOA was collected onto Teflon filters once the aerosol volume concentration stabilized. Even though organic carbon denuders were not used in the collection of the Teflon filters, our previous chemical ionization mass spectrometry measurements indicate that IEPOX is completely removed from the gas phase in the presence of acidified sulfate seed aerosol before the initiation of filter sampling (4). As a result of the latter, the particle-phase IEPOX measured from the Teflon filters is not a result of the absorption of gas-phase IEPOX to the filters during chamber aerosol sampling. The laboratory-generated isoprene SOA provides the particle-phase IEPOX standard necessary for comparison to the atmospheric samples collected from the AMIGAS campaign.

2,3-epoxy-1,4-butanediol (BEPOX) was used as a surrogate standard to quantify the particle-phase IEPOX detected in the atmospheric aerosol. For the BEPOX synthesis, an aqueous solution of 2-butene-1,4-diol (Fluka, purum, ≥ 98.0%) was reacted with H$_2$O$_2$ catalyzed by tungstic acid, followed by removal of water and other impurities (3, 12). Nuclear magnetic resonance (i.e., ‘H NMR) study of the final product revealed a purity >95%. A BEPOX-derived organosulfate was used as a surrogate to quantify the organosulfate derivatives of the 2-methyltetrols. The BEPOX-derived organosulfate was prepared by reacting BEPOX with H$_2$SO$_4$ and Na$_2$SO$_4$ in aqueous solution. The concentration of the BEPOX-derived organosulfate in the solution was determined by $^1$H NMR.

Prior to methanol extraction, the filters were spiked with cis-ketopinic acid as an internal recovery standard; cis-ketopinic acid was chosen since it was not found in the ambient samples and did not overlap with the targeted compounds. The field and laboratory samples were chemically characterized by both GC/TOFMS and GC/MS with prior trimethylsilylation; these techniques were both equipped with an electron ionization (EI) source. A detailed description of the sample preparation protocols and the GC/MS analyses is provided by Suratt et al. (4). For the GC/TOFMS analysis, the samples were analyzed by an Agilent 6890N gas chromatograph (GC DB-5MS column (30 m x 0.25 mm ID x 0.25 μm thickness)) coupled to a Waters GCT Premier TOF mass spectrometer, allowing for accurate mass measurements (i.e., determination of molecular formulas) to be obtained for each observed ion. Further operating details of the GC/TOFMS technique can be found in Kautzman et al. (13).

The GC/TOFMS analysis was conducted to determine the elemental compositions of the fragment ions produced from the trimethylsilylated IEPOX, allowing preparation of a fragmentation scheme for the latter. The GC/MS analysis was conducted to quantify IEPOX, 2-methyltetrols, C$_4$-alkenetriols, and 2-methylglyceric acid products by using the peak areas derived from the total ion chromatograms (TICs). From the repeated GC/MS measurements of the C$_4$-tetrol and BEPOX standards, the variation in the intensity is about 2-3%. IEPOX has been detected in laboratory-generated isoprene SOA using the GC/MS with prior trimethylsilylation (4). As previously observed by Suratt et al. (4), the mass spectral fragmentation of BEPOX is similar to that of IEPOX, making BEPOX a suitable surrogate standard to quantify particle-phase IEPOX. Although an epoxide could potentially be considered as a labile molecule in the GC/MS analysis, trimethylsilyl derivatives of isoprenoid glycidic ethers containing a 2,3-epoxy-1-ol moiety have been previously observed using GC/MS techniques (14). Additionally, Yu and Jeffries (15) reported that the epoxy carbonyl products of toluene photooxidation, as well as a commercially available epoxy carbonyl (i.e., 1,2-epoxy-3-cyclohexanone) standard, could be successfully derivatized by PFBHA (O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine) in an aqueous solution and detected by GC/MS. In combination with the fact that we observe the BEPOX standard, these two prior studies further support the ability of observing epoxides by GC/MS techniques.

During GC/MS analyses, the dehydration of the BEPOX standard to C$_4$-alkenetriols was not observed in the calibration experiments. The conversion of BEPOX standard to C$_4$-tetrols was not significant (~1% of BEPOX was converted to C$_4$-tetrols). It is likely that the conversion of IEPOX to 2-methyltetrols and C$_4$-alkenetriols was not significant in the GC/MS analyses. The laboratory and field blank filters (day and night) were analyzed identically. Isoprene SOA tracers, including IEPOX, were not detected from these blank filters. Organic carbon denuders were not used for the collection of these samples owing to the design of the PM$_{2.5}$ inlet on the high-volume filter samplers (Tisch Environmental, Cleves, OH), and thus, some fraction of the measured particle-phase IEPOX mass concentration could be partly due to the gas-phase absorption of IEPOX onto the quartz filter media.

Samples were also analyzed by ultra performance liquid chromatography/electrospray ionization-time-of-flight mass spectrometry (UPLC/ESI-TOFMS) operated in the negative (-) ion mode in order to quantify the organosulfates of the 2-methyltetrols found in the AMIGAS aerosol samples. From
the repeated UPLC/ESI-TOFMS measurements of the BE-POX-derived organosulfate standard, the variation in the intensity is about 3%. It should be noted that nitrated organosulfates of isoprene, which are isoprene SOA high-NO\textsubscript{x} tracers, and organosulfates of monoterpenes previously characterized by Surratt et al. (16) were also observed in these samples using the UPLC/(-)ESI-TOFMS technique; however, they will not be discussed in detail in the present manuscript.

Results and Discussion

Quantification and Characterization of IEPOX. Figure 1a shows the extracted ion chromatogram (EIC) of m/z 262 for two trimethylsilyl derivatives of IEPOX (MW 262) from laboratory-generated isoprene SOA formed under low-NO\textsubscript{x} conditions. These two compounds have similar EI mass spectra (Figure 1b and c) as the particle-phase IEPOX recently reported by Surratt et al. (4). The interpretation of the fragment ions in the EI mass spectra of the trimethylsilylated IEPOX is given in Scheme 1. The elemental compositions obtained for the fragment ions measured by the GC/TOFMS technique (see SI Tables S2 and S3) support the proposed ion structures in the fragmentation scheme. The EI mass spectra obtained for the two chromatographic peaks are very similar though there are some differences in the relative abundance of m/z 147, which is characteristic of the presence of two trimethylsiloxy groups. We thus assign the IEPOX isomers to enantiomeric forms (i.e., threo and erythro) of the same positional isomer, 2R,3R (threo), 2S,3S (threo), 2S,3R (erythro), and 2R,3S (erythro). The threo and erythro forms have different shapes and will be separated upon GC, while the

FIGURE 1. GC/TOFMS data for trimethylsilylated IEPOX (MW 262): (a) EIC of m/z 262 for particle-phase IEPOX formed from the photooxidation of isoprene under low-NO\textsubscript{x} conditions in the presence of acidified sulfate seed aerosol, (b) EI mass spectrum for the chromatographic peak at retention time (RT) = 23.23 min, (c) EI mass spectrum for the chromatographic peak at RT = 23.73 min, (d) EIC of m/z 262 for IEPOX detected during the daytime on August 9, 2008 at the JST site, (e) EI mass spectrum for the chromatographic peak at RT = 23.35 min, (f) EI mass spectrum for the chromatographic peak at RT = 23.86 min. The ion at m/z 227 in the mass spectra obtained for the ambient sample (1e and 1f) is most likely due to coelution from an interfering compound.

SCHEME 1. Proposed Fragmentation Pathways of Trimethylsilylated 2,3-Epoxy-2-Methyl-1,4-Butanediol (Threo and Erythro Forms) upon Electron Ionization-Mass Spectrometry

The same reactions at the other side of the molecular ion lead to the m/z 131, 130, and 115 ions in the case of pathway (A) and to the very minor m/z 204 ion in the case of pathway (B).
two stereoisomers of each form will not be separated since they are mirror images. The \( m/z \) 147 ion points to the presence of two trimethylsilyloxy groups in the molecules and can be explained through formation of an ion-neutral complex in which the trimethylsilyl ion (formed by a heterolytic cleavage of an ionized O–Si bond) migrates to a nucleophilic position in the molecule, i.e., the second trimethylsilyloxy group (17). This group is closer in the erythro form than in the threo form (Scheme 2), resulting in an

\[ \text{Scheme 2. Proposed Formation of the } m/z \text{ 147 Ion in the EI Mass Spectra of the Trimethylsilyl Derivatives of the Erythro and Threo Forms of 2,3-Epoxy-2-Methyl-1,4-Butanediol} \]

For example, Surratt et al. (4) observed that the mixing ratio of gas-phase IEPOX did not change in the presence of dry ammonium sulfate seed aerosol with an organic mass loading of 1.7 \( \mu \)g m\(^{-3}\) in the chamber study. IEPOX is highly soluble in \( H_2O \) (3). The Henry’s law constant, \( H \), of IEPOX was estimated using the HenryWin v3.2 (19). 1,4-Butanediol was chosen as the base compound, the estimated \( H \) value of which at 298 K ranges from \( 1.0 \times 10^3 \) to \( 5 \times 10^6 \) M atm\(^{-1}\) using a group contribution method (20). IEPOX is estimated to have an \( H \) value ranging from \( 1.9 \times 10^5 \) to \( 9.6 \times 10^6 \) M atm\(^{-1}\) at 298 K. Despite the uncertainties, these estimates suggest that the presence of particle-phase IEPOX may be attributable to the absorption into the aqueous phase of preexisting aerosol. It is noted that once gas-phase IEPOX partitions into the particle phase, depending on the aerosol composition (e.g., aerosol acidity), IEPOX can be hydrolized to form isoprene SOA tracers (e.g., 2-methyltetros and their corresponding hydroxy sulfate esters). The hydrolysis rate of IEPOX is expected to be similar to that of 1,2-epoxy-3,4-dihydroxybutane (\( k = 0.0012 \) M\(^{-1}\) s\(^{-1}\), 1 M \( \text{Na}_2\text{SO}_4/0.2 \) M \( \text{D}_2\text{SO}_4/\text{D}_2\text{O} \) solution), which has a lifetime of 7.7 h at \( pH = 1.5 \) and a lifetime of 38 days at \( pH = 4.0 \) (5). Thus, incompletely reacted IEPOX in the particle phase might explain the presence of IEPOX in ambient aerosol. In fact, Surratt et al. (4) previously demonstrated that the reactive uptake of gas-phase BEPOX in the presence of acidified sulfate seed aerosol yielded some fraction of incompletely reacted particle-phase BEPOX, as detected by GC/MS.
The catalyzed ring-opening of IEPOX followed by the subsequent formation of the 2-methyltetrols is likely attributed to the acid-catalyzed dehydration of the BEPOX to the C4-alkenetriols was detected since epoxide intermediates react more efficiently with H2SO4 to form organosulfates than alcohol intermediates (5, 21), formation of the 2-methyltetrols and the organosulfate derivatives of the 2-methyltetrols is likely attributed to the acid-catalyzed ring-opening of IEPOX followed by the subsequent nucleophilic addition of H2O and inorganic sulfate (4). In addition to previously suggested gas-phase oxidation pathways (22), the 2-methyltetrols can form from the heterogeneous reactions of IEPOX as discussed above. The measured 2-methyltetrol concentrations could be influenced by acid-labile derivatives of the 2-methyltetrols, such as sulfate and nitrate esters and may not be stable upon trimethylsilylation, and as result, a fraction of these derivatives of the 2-methyltetrols may be measured as 2-methyltetrols by GC/MS techniques (4, 23).

Daytime and nighttime samples from two sites are combined for correlation analysis, excluding the one sample at YRK (September, 6, 2008, nighttime), in which IEPOX and C5-alkenetriols were not detected. Despite the limited sample size (N = 15), the correlation between the measured isoprene SOA tracers and IEPOX can be evaluated. As expected, the isoprene SOA tracers are positively correlated with each other, and the degree of correlation between these tracers may give some insight into their formation pathways. IEPOX is well correlated with the 2-methyltetrols (R2 = 0.78), is fairly well correlated with the organosulfates of the 2-methyltetrols (R2 = 0.41), but exhibits a weaker correlation with 2-methylglyceric acid (R2 = 0.21). IEPOX correlates well with the organosulfates of the 2-methyltetrols when considering the two sites separately (R2 = 0.95 at JST and R2 = 0.86 at YRK). Compared to IEPOX, 2-methylglyceric acid shows a weaker correlation with other known isoprene SOA tracers (2-methyltetrols: R2 = 0.16, and organosulfates of 2-methyltetrols: R2 = 0.28). This is likely a result of the fact that IEPOX is a gas-phase precursor for these tracers (4). In addition, 2-methylglyceric acid (and its corresponding oligoesters) is formed more efficiently from the photooxidation of isoprene under high-NOx conditions (i.e., high NO2/NO ratios), while IEPOX is formed more efficiently under low-NOx conditions (i.e., high HNO3/NO ratios) (3, 4). The latter is due to the fact that IEPOX formation occurs only under conditions when RO2 radicals react primarily with H2O rather than with NO (3, 4).

Although IEPOX is weakly correlated with C5-alkenetriols (R2 = 0.25) in the combined data set, a high correlation between IEPOX and C5-alkenetriols was observed when considering the two sites separately (R2 = 0.98 at JST and R2 = 0.92 at YRK). During GC/MS analyses, neither the dehydration of the C5-tetrols into the C5-alkenetriols nor the dehydration of the BEPOX to the C5-alkenetriols was detected.
in the calibration experiments. Consequently, the formation of the C5-alkenetriols from the dehydration of 2-methyltetrols and IEPOX in the GC/MS analysis is likely not significant. Also, a lower correlation between C5-alkenetriols and 2-methyltetrols (R² = 0.63 at JST and R² = 0.85 at YRK) was observed. It is likely that the C5-alkenetriols are not artifacts and the sample size is limited, a high correlation between the C5-alkenetriols and IEPOX in ambient samples suggests that the dehydration of IEPOX in acidic aerosol, as proposed by Wang et al. (24), is a potential formation pathways of C5-alkenetriols.

IEPOX is known to be rapidly removed from the gas phase by pre-existing acidified sulfate seed aerosol to form low-NOx SOA and is likely dissolved into the aqueous phase of the particles. The IEPOX will continuously react in the particle phase once it dissolves into the aqueous phase. Since the filter samples were collected over 8 h integrated time periods, it does not allow us to correlate the measured particle-phase IEPOX mass concentrations (and its known reaction products) with an estimate of liquid water content of the aerosol or aerosol acidity. Higher time resolution data would provide more useful insights.

**Atmospheric Abundance and Implications.** Table 1 shows the measured mass concentrations of isoprene SOA tracers at two sites. The mean mass concentration of the 2-methyltetrols is 56 ng m⁻³ at JST (range: 17–126 ng m⁻³) and 98 ng m⁻³ at YRK (range: 10–216 ng m⁻³). By comparison, Ding et al. (25) reported that the mass concentration of the 2-methyltetrols, on average, was 55.1 ng m⁻³ with a maximum mass concentration of 467 ng m⁻³ in their 24 h integrated filter samples of fine ambient aerosol collected at the JST site from May 2004 to April 2005. Isoprene-derived organosulfates have been detected in both laboratory-generated SOA and ambient aerosol collected from the southeastern U.S (16). Among the isoprene-derived organosulfates, the organosulfates of the 2-methyltetrols usually exhibit the largest UPLC chromatographic peak in daytime samples (data not shown); however, individual organosulfates have not been quantified owing to the lack of appropriate standards. Using the synthesized BEPOX-derived organosulfate standard, the mass concentration of the organosulfate derivatives of the 2-methyltetrols ranged from 6.7 to 64 ng m⁻³ at JST and from 5.1 to 46 ng m⁻³ at YRK, levels at which these ambient tracers for isoprene SOA formation are significant components of fine ambient aerosol formed in the southeastern United States. As observed in the laboratory chamber experiments, the oxidation of SO₂ forms sulfuric acid, which provides the hydrogen ions and sulfate ions necessary for the formation of organosulfates in the atmosphere. We detected 2-methylglyceric acid, as well as nitrated organosulfates of isoprene, which are formed from the photooxidation of isoprene in the presence of NOₓ (16, 26) and are known as isoprene SOA high-NOₓ tracers. This suggests the isoprene SOA is formed via both the low- and high-NOₓ pathways. On average, the sum of the mass concentrations of IEPOX and the measured isoprene SOA tracers (2-methyltetrols, C5-alkenetriols, and 2-methylglyceric acid) were found to account for about 3% of the organic carbon at JST and YRK, respectively. It is also noted that acid-labile derivatives of the 2-methyltetrols such as sulfate and nitrate esters may not be stable upon trimethylsilylation and may be measured with the GC/TOFMS and GC/MS techniques as 2-methyltetrols (23). The secondary organic carbon (SOC) contributions from isoprene oxidation can be estimated using the tracer method developed by Kleindienst et al. (27). Using the tracer concentrations (i.e., 2-methyltetrols and 2-methylglyceric acid) and the laboratory-derived tracer mass fraction (0.155), the mean SOC contributions from isoprene oxidation were estimated to be 0.4 µg C m⁻³ (range: 0.2–0.9 µg C m⁻³) at JST and 0.7 µg C m⁻³ (range: 0.1–1.4 µg C m⁻³) at YRK. These values are comparable to those observed by Kleindienst et al. (27) from Research Triangle Park, North Carolina, U.S. during August and September, 2003 (mean: 0.7 µg C m⁻³; range: 0.2–1.5 µg C m⁻³) and are higher than those observed by Kourtchev et al. (28) from K-puszta, Hungary (mean: 0.28 µg C m⁻³) and by Hu et al. (29) from Hong Kong, China during summer period (mean: 0.2 µg C m⁻³; range: 0.01–0.81 µg C m⁻³). Overall, these results suggest that isoprene oxidation is important to the formation of fine ambient aerosol in this region.

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**Note Added after ASAP Publication**

Due to a production error, this paper published ASAP May 17, 2010 with errors in the text and Table 1; the corrected version published ASAP May 21, 2010.

**Supporting Information Available**

Averaged gas-phase concentrations of O₃, CO, SO₂, and NOₓ during the sampling period are given in Table S1. The elemental compositions obtained for the major fragment ions in Figure 1 measured by the GC/TOFMS technique are given in Tables S2–S5. This material is available free of charge via the Internet at http://pubs.acs.org.

**Literature Cited**


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