**One-sentence Summary:**

Novel polar organic compounds, i.e., 2-methylthreitol and 2-methylerythritol, were observed in significant concentrations in natural tropical aerosols and linked to the photo-oxidation of isoprene, which seems to be an important global source of biogenic secondary organic aerosol.

# Formation of Secondary Organic Aerosols through Photo-Oxidation of Isoprene

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**Detailed organic analysis of natural aerosols from the Amazonian rain forest showed significant quantities of novel polar organic compounds that were identified as a mixture of diastereoisomeric 2-methyltetrols, i.e., 2-methylthreitol and 2-methylerythritol. These polyols, which have the isoprene skeleton, can be explained by OH radical-initiated photo-oxidation of isoprene. They have low vapor pressure, so that they can condense onto pre-existing particles. It is estimated that photo-oxidation of isoprene results in an annual global production of about 2 Tg of the polyols, a significant fraction of the IPCC estimate of between 8 and 40 Tg per year of secondary organic aerosol from biogenic sources.**

Aerosols are of climatic interest because they act as cloud condensation nuclei (*1*) and scatter and absorb solar radiation (*2*). It has been well established that photo-oxidation products of monoterpenes (e.g., α- and β-pinene) (*3, 4*), biogenic volatile organic compounds (VOCs) emitted mainly by terrestrial vegetation, contribute to the aerosol budget (*5, 6*). The much larger emissions of isoprene (*7*), however, are assumed not to result in secondary organic aerosol (SOA) formation in the atmosphere (*8*). Knowledge of the degradation mechanisms of isoprene, which represents on the global scale almost 50% of all biogenic non-methane hydrocarbons (*7*), is of considerable interest for air quality modeling (*9*). It has recently been proposed that heterogeneous reaction of isoprene on acidic particles could be an important source of humic-like substances, which contribute 20-50% of the water-soluble organic aerosol at urban and rural sites in

Europe (*10*). Here we report evidence that photo-oxidation of isoprene is a significant source of SOA, contrary to previous assumptions.

As part of the LBA-CLAIRE-1998 and -2001 experiments (CLAIRE = Cooperative LBA Airborne Regional Experiment; LBA = The Large Scale Biosphere-Atmosphere Experiment in Amazonia), atmospheric aerosols were collected at Balbina (1º55'S, 59º24'W), 125 km north of Manaus, Brazil, during the wet season (*11*). Backward air mass trajectories indicated that this site was not affected by anthropogenic sources, as surface air masses originated from the northeast to east, and, hence, had traveled a thousand kilometers over the most remote regions of the Amazonian rain forest for almost a week before being sampled. The organic compounds present in the aerosol samples are, therefore, believed to be characteristic of local and regional atmospheric chemical phenomena rather than of long-range transport. The Amazon basin contains the world's largest humid forest ecosystem, known to emit large quantities of VOCs (*7, 12*). Since solar radiation and the production of OH radicals are at maximum in the tropics, the formation of photo-oxidation products from natural VOCs is expected to be important.

Selected aerosol samples were subjected to analysis by gas chromatography/mass spectrometry (GC/MS) for detailed characterization of organic compounds (*11*). Fig. 1 presents a GC/MS total ion current (TIC) chromatogram of the trimethylsilylated (TMS) extract of the fine size fraction (PM2.5: particulate matter with diameter <2.5 µm) of a typical aerosol sample collected during the CLAIRE-2001 campaign with a high-volume (Hi-Vol) air sampler. Compounds **1** and **2** correspond to the newly found compounds,

which were identified as diastereoisomeric forms (*threo* and *erythro*) of a polyol, i.e., 2-methylthreitol and 2-methylerythritol. The structures of these compounds were elucidated using a combination of electron ionization (EI) and methane chemical ionization (CI) GC/MS, and then confirmed by comparison of the GC/MS data with those of synthesized reference compounds (*11*). Mass spectra of the TMS derivatives of compounds **1** and **2** are shown in Figs. S1 and S2, while those of the synthesized reference compounds are given in Fig. S3.

Taking into account that 2-methylthreitol and 2-methylerythritol have the $C_5$ isoprene skeleton, it is logical to propose that isoprene is the precursor for their formation in the atmosphere. To date, the photo-oxidation of isoprene in the atmosphere has been believed to result only in volatile products, in particular formaldehyde, methacrolein and methyl vinyl ketone, and not in condensable products that can be found in the aerosol phase. A primary plant origin of the 2-methyltetrols could be ruled out because they are not known to be present in plant leaves (*13*), were not found in a composite sample of leaves from Amazonian tree species (*11*), and occur as a mixture of diastereoisomers, consistent with a non-enzymatic formation process. Since the 2-methyltetrols are not of primary biogenic origin, they have to be considered as secondary organic aerosol components. The 2-methyltetrols have, to our knowledge, not been reported before, either in chamber experiments with isoprene or from ambient aerosols. A possible reason why they have not been detected in earlier aerosol composition studies is that the methods generally used are targeted to the determination of dicarboxylic acids. These methods are based on methylation of carboxylic groups and GC/MS, or on direct liquid

chromatography/MS with electrospray ionization in the negative ion mode, and are not well suited to the analysis of neutral polyols.

Chamber experiments with isoprene under simulated atmospheric conditions have generally been performed in the presence of relatively high levels of ozone and $NO_x$ (*8*), conditions that are different from natural tropical atmospheric conditions, which, except in the burning season, are characterized by low $NO_x$ concentrations ((NO) <100 ppt) (*14*). It is known that photo-oxidation of isoprene is dominated by its reaction with OH radicals, since its reaction with ozone is relatively slow (*15*). When the OH radical-initiated photo-oxidation of isoprene has been investigated in the absence of $NO_x$, aerosol formation has been noted (*8*) and, furthermore, the formation of 1,2-diol derivatives, i.e., 2- and 3-methyl-3-butene-1,2-diol, has been demonstrated (*16*). For the formation of the 1,2-diols, a reaction mechanism involving reaction with $HO^{\bullet}/O_2$ followed by self and cross reactions of peroxyradicals ($RO_2^{\bullet}$) has been proposed (*16*). The formation of the 2-methyltetrols from isoprene in the present study under tropical atmospheric conditions can be explained by two cycles of these reactions (Scheme 1) (further discussion of potential formation mechanisms is given in Supporting Online Material (SOM) text). The yield of the 2-methyltetrols from isoprene oxidation of 0.2% (0.4% in mass terms) (*vide infra*) is consistent with the low aerosol carbon yields in chamber experiments (*8*). The vapor pressures of the 2-methyltetrols are expected to be very low ($<1.6 \cdot 10^{-5}$ Torr, the value calculated for 2,3,4-pentanetriol at 27°C), so that these products are expected to be predominantly in the condensed phase (*17*). A gas-to-particle transfer mechanism, most

likely condensation onto pre-existing particles, operates in aerosol formation from

2-methyltetrols (*vide infra*).

The 2-methyltetrols, 2-methylthreitol and 2-methylerythritol, are expected to be

hygroscopic and to have a water solubility comparable to those reported for racemic

D,L-threitol (i.e., 8.8 g ml$^{-1}$ water) and meso-erythritol (i.e., 0.64 g ml$^{-1}$ water),

respectively (*18*). The hygroscopic growth of submicrometer aerosol particles has been

studied using tandem differential mobility analysis at the same remote rain forest site in

central Amazonia during the LBA-CLAIRE-1998 campaign (*19*). In that study,

hygroscopic particles could be identified that were typical of the pristine rain forest

atmosphere and were believed to contain oxidation products of biogenic compounds. In

addition, it has been demonstrated that most aerosol particles contain enough water-

soluble material to be able to act efficiently as cloud condensation nuclei (*20*).

In addition to the 2-methyltetrols, the extract of the fine size fraction of the wet

season aerosols also contained other oxygenated organic compounds, i.e., mono- and

dihydroxydicarboxylic acids and polysaccharidic compounds (Fig. 1). The mono- and

dihydroxydicarboxylic acids and saccharidic compounds were identified by comparing

their EI mass spectra and GC behaviors with those of authentic standards. The mono- and

dihydroxydicarboxylic acids included malic acid, α-hydroxyglutaric acid, tartaric acid,

and novel minor compounds, which occurred as a mixture of diastereoisomers (*threo* and

*erythro*) and were tentatively identified as 2,3-dihydroxyglutaric acids (Fig. 1;

compounds **4** and **6**) (*11*). The major identified saccharidic compounds were

levoglucosan, arabitol, mannitol and glucose. Of the mono- and dihydroxydicarboxylic

acids, malic, tartaric and α-hydroxyglutaric acid have been previously reported in

Amazonian aerosols at appreciable atmospheric concentrations (>10 ng m$^{-3}$) (*21*). As to

the atmospheric origin of these compounds, malic acid has been proposed to be a late

product in the photochemistry of unsaturated fatty acids (*22*), but other biogenic sources,

such as *n*-alkanes emitted by the forest vegetation, could also be considered. The other

mono- and dihydroxydicarboxylic acids, tartaric acid, α-hydroxyglutaric acid, and the

2,3-dihydroxyglutaric acids, likely have the same atmospheric origin as malic acid.

Levoglucosan (1,6-anhydro-β-D-glucopyranose) is a molecular marker for biomass

burning (*23*), which has proven its usefulness for monitoring biomass burning in

Amazonian aerosols (*21, 24*). The sugar alcohols, arabitol and mannitol, are attributed to

natural background and are believed to originate from fungal spores, whereas the

monosaccharide, glucose, a common plant sugar, is likely due to pollen (*25*).

In order to determine whether compounds were associated with fine or coarse

mode particles, we analyzed a set of fine and coarse filter samples from day and

nighttime collections during LBA-CLAIRE-2001. Quantitative determinations of the

2-methyltetrols, mono- and dihydroxydicarboxylic acids, and saccharidic compounds

were performed by gas chromatography-flame ionization detection (GC-FID) (Table 1)

(*11*). The results obtained for the 2-methyltetrols show that they are enriched in the fine

size fraction, suggesting that they are SOA components, i.e., formed by gas-to-particle

conversion processes. The presence of 2-methyltetrols, formed by daytime photo-

oxidation of isoprene, at a significant concentration in the nighttime sampling can be

explained by the high chemical stability of the 2-methyltetrols and the lower nighttime

temperatures, which favor condensation onto particles. Table 1 also shows that the

2-methyltetrols explain about 2% of the organic carbon (OC) in PM2.5 aerosols.

Similarly, the mono- and dihydroxydicarboxylic acids, malic acid, $\alpha$-hydroxyglutaric

acid, the 2,3-dihydroxyglutaric acids, and tartaric acid, are enriched in the fine size

fraction, as expected for SOA components. Levoglucosan, a primary organic aerosol

component and a molecular marker for wood combustion (*23*), is associated with the fine

size fraction, consistent with formation by a high temperature combustion process. In

contrast, the sugar alcohols, arabitol and mannitol, and the sugar, glucose, are enriched in

the coarse size fraction, as could be expected for compounds typical of fungal spores and

plant pollen (*25*). It is seen from Table 1 that the atmospheric concentration of the

2-methyltetrols is larger than that of malic acid, which was found to be the major

hydroxydicarboxylic acid. The concentration of the 2-methyltetrols was comparable to

that of oxalic acid, a dicarboxylic acid which is typically the major water-soluble organic

species identified in atmospheric aerosols (*26*). The concentration of oxalic acid during

the LBA-CLAIRE-2001 campaign was on average 57 ng m$^{-3}$ for the fine size fraction

and 63 ng m$^{-3}$ for the coarse fraction (*25*).

The atmospheric concentrations of the 2-methyltetrols, malic acid, levoglucosan,

arabitol, mannitol, and glucose in ten selected total filter samples from the LBA-

CLAIRE-1998 wet season campaign are provided in Table S1. During the 1998

campaign the atmospheric concentration of levoglucosan was quite low (average, 0.46 ng

m$^{-3}$; range, 0 - 3.0 ng m$^{-3}$), indicating clean air conditions that were not affected by

biomass smoke. The combined atmospheric concentration of the two 2-methyltetrols and

their percentage relative to the OC mass were 31 ng m$^{-3}$ and 0.61±0.39%, respectively, and, as for the 2001 campaign, higher than those of malic acid (7.2 ng m$^{-3}$ and 0.10±0.06%, respectively).

In a study on VOCs performed at the same remote site in the Amazonian rain forest during the 1998 campaign (*12*), isoprene and its photo-oxidation products were measured, and it was concluded that isoprene chemistry can be regarded as a dominant process within this area. The isoprene mixing ratios were between 4 and 10 ppb, while those of the major photo-oxidation products of isoprene, methacrolein and methyl vinyl ketone, were always significantly below 1 ppb, pointing to a low oxidation capacity of the pristine atmosphere over the Amazonian rain forest, which is in agreement with ozone concentrations that were always below 20 ppb. The median combined atmospheric concentration of the 2-methyltetrols found in the present work was 31 ng m$^{-3}$, or 10 ppt, corresponding to about 0.2% of the isoprene mixing ratio (calculated for a mixing ratio of 5 ppb). It can thus be concluded that aerosol formation from isoprene has a low yield, but considering the large amounts of isoprene that are emitted by the rain forest vegetation, this source may be very important for SOA formation. The apparent yield of 0.2% (0.4% in mass terms) of the 2-methyltetrols can be used to estimate the global contribution of isoprene oxidation to SOA formation (see SOM text). An annual global emission of isoprene of about 500 Tg (*7*) suggests a SOA source strength of about 2 Tg, which can be compared with the IPCC (*27*) estimate of between 8 and 40 Tg per year of SOA from biogenic sources.

Our results indicate that natural aerosols collected in Amazonia, Brazil, contain significant amounts of the 2-methyltetrols, 2-methylthreitol and 2-methylerythritol, which can be explained by OH radical-initiated photo-oxidation of isoprene, as well as smaller amounts of mono- and dihydroxydicarboxylic acids. The 2-methyltetrols were identified as major oxygenated organic compounds in the fine size fraction, and it is estimated that they represent a SOA source strength of about 2 Tg per year. These compounds have low vapor pressure and are hygroscopic, and can, therefore, contribute to particle growth (*28*), enhance the ability of aerosols to act as cloud condensation nuclei, and result in formation of haze (*29*) above forests. The 2-methyltetrols can be regarded as specific molecular markers for the photo-oxidation of isoprene in the ambient atmosphere and are, as such, of potential interest for source apportionment and air quality modeling studies. Contrary to widespread assumption, we suggest that photo-oxidation of isoprene emitted by forest vegetation results in significant SOA formation.

**References and notes**
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**Supporting Online Material**
www.sciencemag.org
Materials and Methods
SOM text
Figs. S1 to S4, and Schemes S1 and S2
Table S1
References

**Table 1.** Concentrations (ng m$^{-3}$) of organic carbon (OC), elemental carbon (EC), polyhydroxylated compounds, and mono- and dihydroxydicarboxylic acids in fine and coarse filter samples from day and night collections with a Hi-Vol dichotomous sampler during the LBA-CLAIRE-2001 wet season campaign in Balbina, Brazil. The percentage carbon contributions to the OC are given in parentheses.

| Time of collection Size fraction | 25-27 July 2001 day | | 25-28 July 2001 night | |
|---|---|---|---|---|
| | fine | coarse | fine | coarse |
| OC | 1550 | 2440 | 830 | 1610 |
| EC | 66 | 28 | 56 | 27 |
| 2-methyltetrols (*threo + erythro*) | 64.7 (1.84) | 40.9 (0.74) | 49.2 (2.62) | -$^{*}$ |
| malic acid | 32 (0.74) | 10.9 (0.16) | 11.6 (0.50) | - |
| α-hydroxy glutaric acid | 16.9 (0.44) | - | 7.1 (0.35) | - |
| 2,3-dihydroxy glutaric acids (*threo + erythro*) | 30 (0.71) | - | 12.0 (0.53) | - |
| tartaric acid | 7.5 (0.15) | - | 3.6 (0.14) | - |
| levoglucosan | 38 (1.10) | - | 12.2 (0.66) | - |
| arabitol | 5.9 (0.17) | 19.1 (0.34) | 9.7 (0.51) | 48 (1.31) |
| mannitol | 9.4 (0.24) | 32 (0.52) | 8.4 (0.40) | 68 (1.68) |
| glucose | 15.6 (0.40) | 134 (2.20) | 0.6 (0.03) | 2.7 (0.07) |

$^{*}$ - denotes that the concentration was less than 10% of that in the fine size fraction; it is not given because of the large associated uncertainty. (Note that the amount on the coarse filter has been corrected for the contribution from fine particles).

**Legends to figure and scheme**

**Fig. 1.** GC/MS total ion current chromatogram obtained for a trimethylsilylated extract of the fine size fraction of a Hi-Vol sample collected during the LBA-CLAIRE-2001 campaign (25-27 July, daytime sampling only). Abbreviations: Mal, malic acid; Lev, levoglucosan; Arab, arabitol; Glu, glucose (2 peaks); Man, mannitol; $C_{16}$, palmitic acid; $C_{18:1}$, oleic acid; and $C_{18}$, stearic acid. Compounds **1** and **2** correspond to the novel 2-methyltetrols, i.e., 2-methylthreitol and 2-methylerythritol, respectively, arising from the photo-oxidation of isoprene.

**Scheme 1.** Proposed formation of the 2-methyltetrols from isoprene by reaction with $OH^{\bullet}/O_2$ followed by self and cross reactions of peroxyradicals. The intermediate 1,2-diols have been reported in chamber experiments with isoprene under low $NO_x$ conditions (*16*).
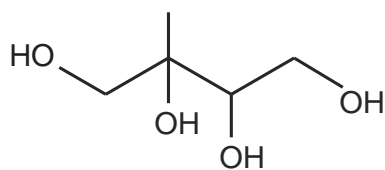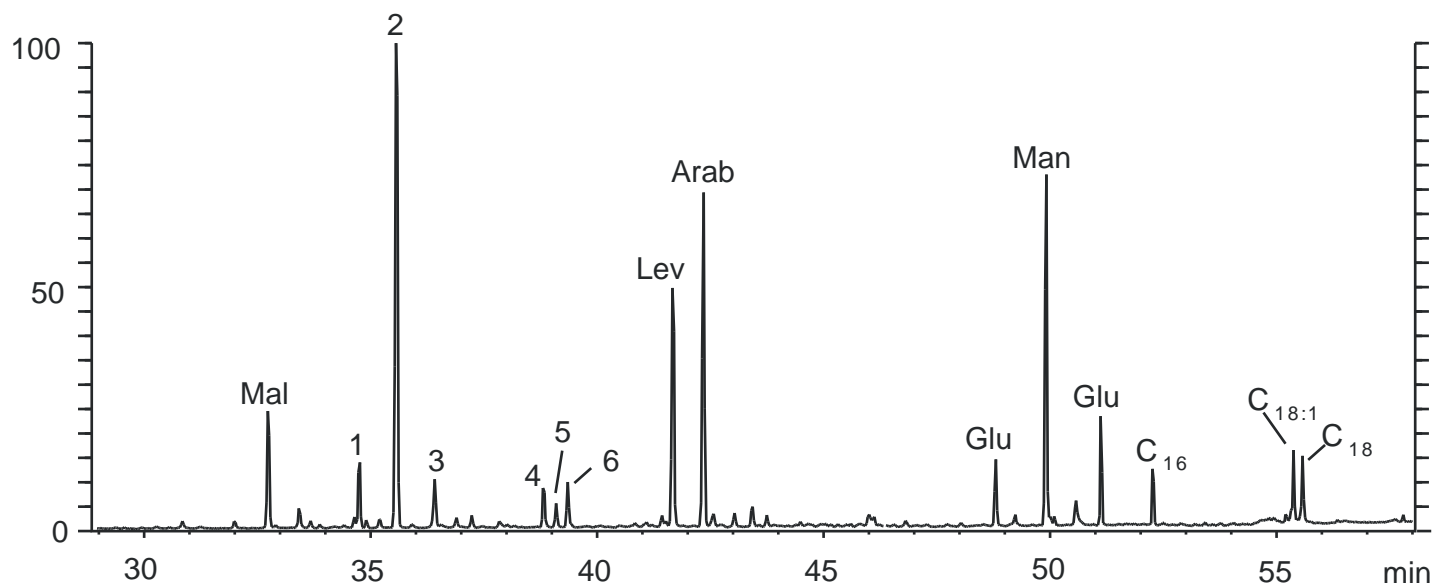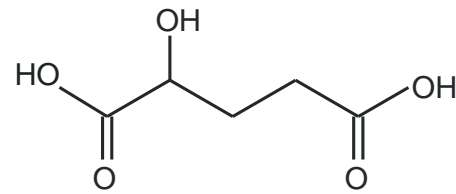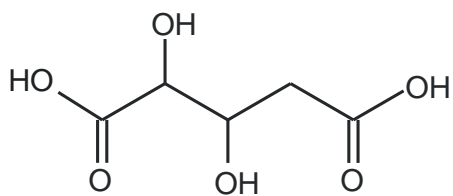
**1** (2-methylthreitol)
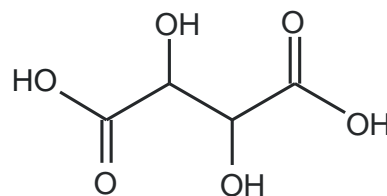**2** (2-methylerythritol)
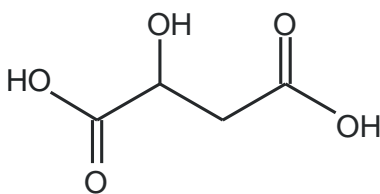
Malic acid

**3** (2-hydroxyglutaric acid)

**4** (2,3-threo-dihydroxyglutaric acid)
**6** (2,3-erythro-dihydroxyglutaric acid)

**5** (tartaric acid)

**(1) OH· / O₂**

**(2) self- and cross reactions**

**2nd cycle (1) + (2)**
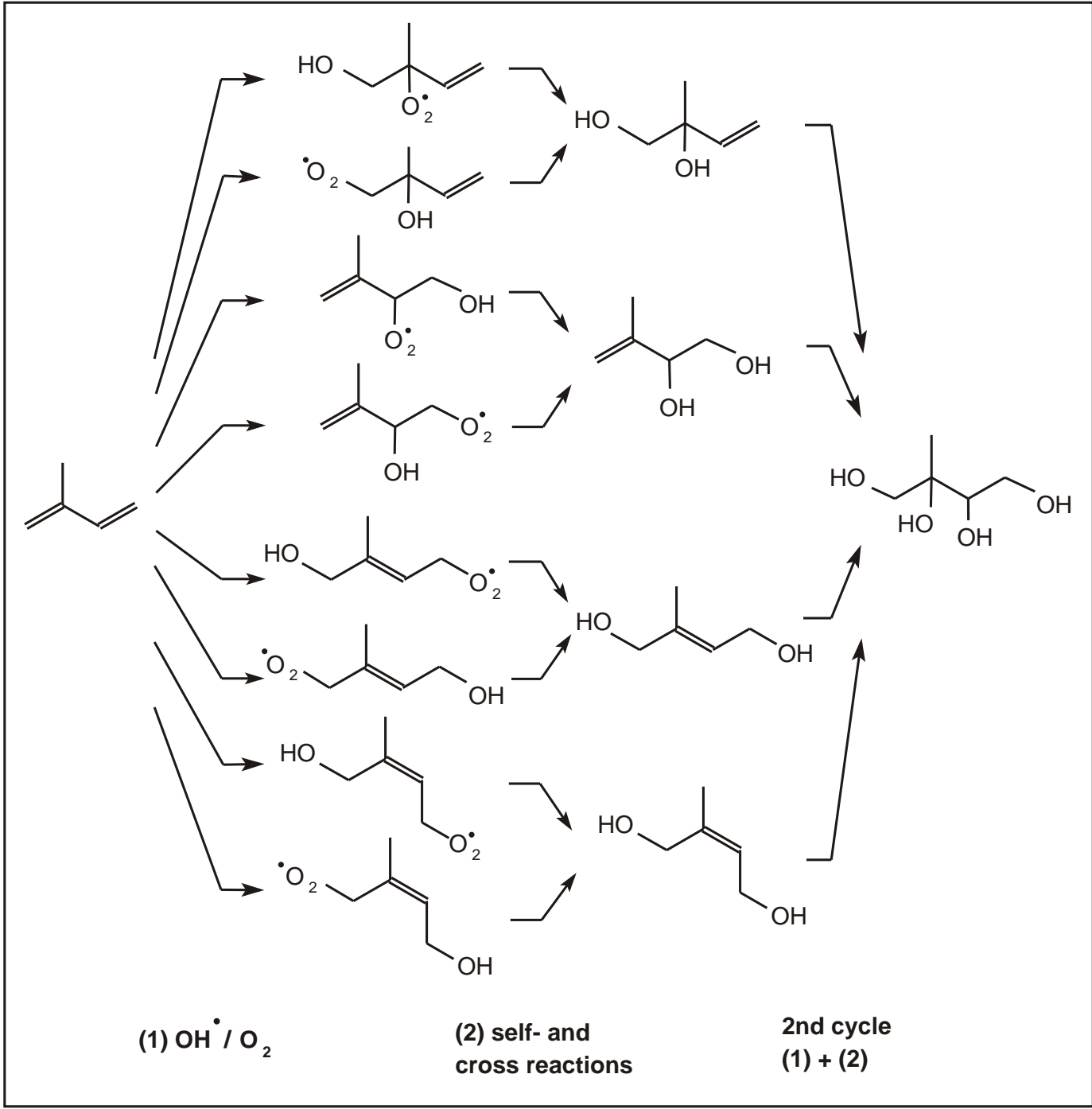
# Supporting Online Material - Science MS# 1092805
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## Materials and Methods

### Aerosol collections and analyses

The collection devices included a total filter sampler in the case of the LBA-CLAIRE-1998 campaign (23 March - 15 April 1998) and a high-volume (Hi-Vol) dichotomous sampler in the case of the LBA-CLAIRE-2001 campaign (11-28 July 2001, period of Hi-Vol sampling). The latter sampler provides a fine (<2.5 µm aerodynamic diameter (AD)) and a coarse (>2.5 µm AD) aerosol size fraction (*S1*). All filters used were quartz fiber filters. Detailed descriptions of the aerosol collection procedures have been reported elsewhere (*S2, S3*). The total filters were weighed before and after sampling to determine the particulate mass (PM). The weighings were done at 20ºC and 50% relative humidity, and the filters were pre-equilibrated at these conditions for at least 24 h before the actual weighings. Furthermore, all total and Hi-Vol filters were subjected to analysis for organic carbon (OC) and elemental carbon (EC) by a thermal-optical transmission technique (*S4*), which delivers OC and EC results in µg(C). The detailed procedure for OC/EC analysis is given in previous articles (*S2, S3*).

**Characterization of organic compounds by GC/MS**

Selected Hi-Vol samples were subjected to GC/MS analysis for characterization of organic compounds. Parts (5 cm$^2$) of the filter samples were extracted with dichloro-methane:methanol (80:20, v/v). A detailed description of the sample work-up and GC/MS procedures has been reported elsewhere (*S5*). Mass spectra were obtained on an Autospec-Ultima instrument (Micromass, Manchester, UK) as well as on a Polaris Q ion trap mass spectrometer (ThermoFinnigan, San Jose, CA, USA). The reference compounds, 2-methylthreitol and 2-methylerythritol (ratio 5/4) were synthesized from 2-methyl-2-vinyloxirane (Sigma-Aldrich, Steinheim, Germany) according to a standard peroxidation/hydrolysis procedure with performic acid (*S6*). The structures of the synthesized 2-methyltetrols were confirmed by 400 MHz $^1$H-NMR spectroscopy.

The unknown compounds **1** and **2** (Fig. 1) were shown to be neutral polyhydroxyl-ated compounds and not mono- or dicarboxylic acids because they failed to form methyl esters with either diazomethane or BF$_3$/methanol. Since the electron ionization (EI) spectra of the trimethylsilyl (TMS) derivatives of compounds **1** and **2** (Fig. S1) and also their methane chemical ionization (CI) spectra (Fig. S2) showed ions at the same m/z values, some of which with different relative abundances, the compounds were charac-terized as diastereoisomers. Detailed analysis of the mass spectra led us to propose 2-methyltetrol, which has a C$_5$ isoprene skeleton. More specifically, this structure proposal was based on characteristic ions in both the EI and CI (methane) mass spectra. The GC retention data were in agreement with diastereoisomeric (*threo* and *erythro*) forms of a C$_5$ tetrahydroxy compound. A mechanistic proposal for the formation of the ions of the TMS derivatives of the 2-methyltetrols (**1** and **2**; Fig. 1) under EI is presented in Scheme S1. The EI mass spectra of the TMS derivatives of the unknown compounds **1** and **2** obtained on the ion trap instrument show an ion at m/z 277 with a greatly increased relative abundance compared to those obtained for the same compounds on the magnetic sector instrument, indicating that this ion is formed by a rearrangement process (Fig. S1; Scheme S1). The CI (methane) mass spectral behavior of compounds **1** and **2** was consistent with that of other polyols, i.e., erythritol and arabitol, in that the ion at the

highest m/z value is the $[MH - CH_4]^+$ ion and fragmentation includes the loss of molecules of TMSOH. The proposed structures were confirmed by comparison of the GC retention data and the EI as well as CI (methane) ion trap mass spectra with those of the synthesized reference compounds (Fig. S3). For the comparison of the GC retention data co-injection with the synthesized reference compounds was performed.

The unknown compounds **4** and **6** were tentatively assigned to diastereoisomeric 2,3-dihydroxyglutaric acids on the basis of the detailed interpretation of the EI mass spectral data of their TMS derivatives. The EI mass spectrum of the TMS derivative of **4** is presented in Fig. S4; an identical spectrum was obtained for **6** except for small differences in the relative abundances of the ions (not shown), consistent with diastereoisomers. The ions employed for the tentative assignment are explained in Scheme S2. Because the unknown compounds **4** and **6** were only minor SOA components their structures were not confirmed using synthesized reference compounds.

**Quantitation of organic compounds by GC-FID**

Selected Hi-Vol and total filter samples were subjected to quantitative analyses by GC-FID. The extraction procedure was the same as given above except that the samples were spiked with an internal recovery standard, i.e., methyl-β-L-xylanopyranoside (Sigma, St. Louis, MO, USA), prior to extraction in order to correct for losses during sample work-up. The quantification was based on the use of response factors relative to methyl-β-L-xylanopyranoside. For the quantification of the 2-methyltetrols, the response factor of erythritol was employed, whereas for that of the mono- and dihydroxydicarboxylic acids other than malic acid, the response factor of the latter was used. The identity of the organic compounds quantitatively determined by GC-FID was subsequently confirmed by GC/MS analysis.

**Analysis of a composite sample of leaves from Amazonian tree species**

A 2-methyltetrol phosphate ester, namely, 2-methyl-D-erythritol-4-phosphate has been reported as a key intermediate in isoprenoid biosynthesis via the novel deoxyxylulose pathway (*S7, S8*). In order to rule out the possibility that the 2-methyltetrols detected in the Amazonian wet season aerosols are due to direct (primary) emission from leaves, a composite sample of leaves from Amazonian tree species was examined for the presence of 2-methyltetrols. Leaves of trees indigenous of the Amazonian rain forest were obtained from the National Botanic Garden of Belgium (Meise); the trees were identified by botanist F. Billiet, and corresponded to the following twelve taxa: *Bombacopsis glabra* (Pasq.) A. Robijns, *Brosium alicastrum* Sw., *Cecropia glaziovii* Snethl., *Couroupita guianensis* Aubl., *Coussapoa microcarpum* (Schott) Rizzini, *Diospyros digyna* Jacq., *Ficus macrosyce* Pittier, *Hymenaea courbaril* L., *Gustavia brasiliensis* C. Morren, *Hevea brasiliensis* Müll. Arg., *Jacaranda mimosifolia* D. Don, and *Muntingia calabura* L. 100 mg (wet weight) of a leaf of each tree taxus was extracted with methanol and further worked up as for aerosol samples. Analysis was performed by GC/MS in the full scan mode employing the conditions used for analysis of aerosol samples. The composite tree leaves sample contained polar carboxylic acids (malic acid and threonic acid) and saccharidic compounds (fructose, glucose, inositol, sucrose and mannitol), but did not reveal 2-methyltetrols.

# Text

**Formation of 2-methyltetrols through OH radical-initiated photo-oxidation of isoprene**

In addition to the formation of the 2-methyltetrols via initial 1,2 $HO^\bullet/O_2$ addition (*S9*), their formation can proceed via initial 1,4 $HO^\bullet/O_2$ addition (*S10*), followed by permutation of the peroxyradicals to form *E*- and *Z*-2-methyl-2-butene-1,4-diol. Similarly to the 1,2-diols, *E*- and *Z*-2-methyl-2-butene-1,4-diol can undergo a second reaction cycle with formation of the target 2-methyltetrols (Scheme S1). The intermediate 2- and 3-methyl-

3-butene-1,2-diols were not detected in our aerosol samples, possibly because these products have a too high vapor pressure and do not condense onto particles. They are very likely present in the air, but in the vapor phase. It should also be realized that the atmospheric concentration of these intermediate products depends upon the reaction rate with which these compounds undergo further oxidation.

The formation of the 2-methyltetrols through OH radical-initiated photo-oxidation of isoprene under conditions of high levels of ozone and $NO_x$ is a subject of further research that is pursued. The importance of the 2-methyltetrol pathway under the latter conditions is currently being investigated using aerosols that were collected in Rondônia, Brazil, during the 2002 dry (biomass burning) season. Preliminary results indicate that 2-methyltetrols are formed. Furthermore, it is worth mentioning that polar organic oxygenates with MS characteristics similar to the 2-methyltetrols identified in the present study were recently reported by Edney *et al.* (*S11*) for PM2.5 aerosols that were collected in a semi-rural forested area in the southeastern USA (i.e., Research Triangle Park, NC). These authors assigned the two major components in the total ion chromatogram (Fig. 2 of *S11*) tentatively to dicarboxylic acids, whereas in our opinion these two components are the same 2-methyltetrols which we identified in our Amazonian aerosols. Thus, it seems that the 2-methyltetrols are also important SOA compounds in forested areas in the USA.

**Yields of the 2-methyltetrols**

The yield of 1,2-diol formation from isoprene in chamber experiments under $NO_x$ free conditions (*S9*) could be used to estimate the likely yield of the 2-methyltetrols from isoprene oxidation in the atmosphere. The yield of the first generation diol products is about 8%. Assuming a similar efficiency of the second cycle would imply a yield of the 2-methyltetrols of about 0.6% v/v, which is in reasonable agreement with the figure of 0.2% v/v stated. There are a number of reasons why the observed figure could be lower. First, the presence of some $NO_x$ lowers the yield of the alkoxyradical permutation reaction products. Secondly, the 2-methyltetrols may not be 100% particle associated.

Finally, the observations reported for the CLAIRE field campaigns were not made under steady state conditions, but with a surplus of locally emitted isoprene, such that the observed quantities of products are lower than predicted. The concentrations of methacrolein and methyl vinyl ketone measured during the 1998 field campaign were all significantly below 1 ppb, as reported by Kesselmeier *et al.* (*S12*). Under steady state conditions, a concentration of 5 ppb isoprene would give rise to concentrations of the order of 2.5 ppb methacrolein and 4 ppb of methyl vinyl ketone (based on molar yields of methacrolein and methyl vinyl ketone of 18% and 15%, respectively, as reported by Ruppert and Becker (*S9*) on the basis of chamber experiments in the absence of $NO_x$, and using the rate constants of Atkinson (*S13*) for the reactions of isoprene and its products with OH). Furthermore, our figure of 0.2% v/v is actually a ratio of mixing ratios; it should be corrected for the loss of isoprene and tetrols in order to convert it into a true production yield.

The tetrol formation yield can be used to estimate the global contribution of isoprene oxidation to SOA formation. The annual global emission of isoprene is about 500 Tg (*S14*). When multiplying this with our uncorrected figure of 0.2% v/v (apparent yield), we arrive at a global production of 2 Tg tetrols per year from isoprene. If instead we replace our apparent yield by the production yield of 0.6% v/v derived on the basis of the chamber experiments of Ruppert and Becker (*S9*), we obtain 6 Tg tetrols per year. Clearly, only a rough estimate of the global production can be given at present. Further laboratory and field measurements will be needed to constrain the estimate.

## Figures and schemes

**Fig. S1.** EI mass spectra obtained for the TMS derivatives of the unknown compounds **1** and **2** (see Fig. 1). (A) **1** and (B) **2** on a magnetic sector instrument; (C) **1** and (D) **2** on an ion trap instrument.

**Fig. S2.** CI (methane) mass spectra obtained for the TMS derivatives of the unknown compounds **1** (A) and **2** (B) (see Fig. 1) on an ion trap instrument.

**Fig. S3.** EI and CI (methane) mass spectra obtained for the TMS derivatives of the synthesized reference compounds, 2-methylthreitol (A) and 2-methylerythritol (B), on an ion trap instrument.

**Fig. S4.** EI mass spectrum obtained for the TMS derivative of the unknown compound **4** (see Fig. 1) on a magnetic sector instrument.

**Scheme S1.** Mechanistic proposal for ions of the TMS derivatives of the 2-methyltetrols (**1** and **2**; Fig. 1) in EI.

**Scheme S2.** Mechanistic proposal for ions of the TMS derivatives of the 2,3-dihydroxy-glutaric acids (**4** and **6**; Fig. 1) in EI.

## Table

**Table S1.** Median concentrations (ng m$^{-3}$) and concentration ranges of PM, OC, EC, polyhydroxylated compounds, and malic acid in 10 total filter samples collected during the LBA-CLAIRE-1998 wet season campaign (23 March - 15 April 1998) in Balbina, Brazil.

| | Concentration (range) | | Mean % carbon of OC |
|---|---|---|---|
| PM | 7500 | (4900-18300) | |
| OC | 2700 | (2100-5300) | |
| EC | 0 | (0-14) | |
| 2-methyltetrols (*threo + erythro*) | 31 | (14-83) | 0.61 ± 0.39 |
| malic acid | 7.2 | (2.6-15) | 0.10 ± 0.06 |
| levoglucosan | 0.46 | (0-3.0) | 0.02 ± 0.02 |
| arabitol | 81 | (42-270) | 1.36 ± 0.43 |
| mannitol | 112 | (58-330) | 1.79 ± 0.38 |
| glucose | 29 | (12-76) | 0.60 ± 0.42 |

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