Chapter 18
Tracers for Biogenic Secondary Organic Aerosol from α-Pinene and Related Monoterpenes: An Overview

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Abstract In this review, we first address the terpenoid composition of ambient fine rural aerosol to give a report on the current state of knowledge in regard to the molecular characterisation of biogenic secondary organic aerosol tracers. The major known, recently elucidated, and still unknown tracers, which can be detected at a significant relative abundance, are listed and briefly discussed. In a second part, we provide a historic account on the discovery of 3-methyl-1,2,3-butanetricarboxylic acid, which involved a long search with several failures and a final success, and propose a revised formation pathway. Finally, we present some brief conclusions and perspectives.

Keywords Alpha-pinene • Ambient fine aerosol • 3-Methyl-1,2,3-butanetricarboxylic acid • Molecular Characterisation • Secondary Organic Aerosol • Terpenylic Acid

18.1 Introduction

Biogenic secondary organic aerosol (SOA) from the oxidation of monoterpenes such as α-pinene is a dynamic and complex mixture [19, 22, 23]. As the SOA evolves or ages due to oxidation reactions, which involve ozone and/or OH or NO_3

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radical-initiated reactions, more oxygenated products are formed with increased hydrophilic properties, enhancing the capability of the aerosol to act as cloud condensation nuclei (for a review, see Ref. [10]). On the other hand, oxidation reactions of semi-volatile precursors in the gas phase may also result in fragmentation to smaller molecules. In addition to gas-phase oxidation reactions, heterogeneous reactions occurring in the particle phase have to be considered; these reactions include esterification with sulfuric acid of hydroxyl- or epoxy-containing SOA products [14, 15, 33–35], esterification of pinic acid with hydroxyl-containing terpenoic acids [4, 28, 38], and OH-initiated oxidation reactions [5].

Despite the fact that biogenic SOA is rather complex, it contains single components at a significant relative abundance that are suitable as molecular markers or tracers for the characterisation of ambient fine aerosol and allow one to gain insights into biogenic volatile organic compound (BVOC) precursors and aerosol formation processes. Since the lifetime of ambient fine aerosol is variable and may be from a few hours to a few days it is useful to have tracers which reflect fresh (unaged) and aged biogenic SOA. Well-established tracers that are known for a long time for fresh α-pinene SOA are pinonic and *cis*-pinic acids (e.g., Refs. [1, 6, 11–13, 41]). However, during the past decade, significant progress has been made with respect to the chemical characterisation of additional α-pinene SOA tracers, including tracers for fresh as well as aged SOA. For example, a novel tracer for fresh α-pinene SOA is terpenylic acid [3], while 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) is a tracer for aged α-pinene SOA [36].

18.2 Monoterpene SOA Tracer Composition of Ambient Fine Rural Aerosol

Figure 18.1 shows selected chromatographic data [base peak chromatogram (BPC) and extracted ion chromatograms (EICs)] for a methanolic extract of K-puszta fine aerosol (PM2.5; particulate matter with an aerodynamic diameter <2.5 μm), which can be regarded as representative for a biogenic SOA-rich aerosol [20]. The extract was obtained from a pooled aerosol sample comprising portions of 5-day- and night-time samplings of the warm period of the 2006 summer campaign [27] and contains fresh as well as aged SOA. The data were obtained using liquid chromatography coupled to negative ion electrospray ionisation mass spectrometry [LC/(-) ESI-MS], following a published procedure [39].

The major tracers that could be detected at a significant relative abundance were:

1. the known α-pinene SOA tracers, *cis*-pinonic acid (MW 184), *cis*-pinic acid (MW 186), and 10-hydroxypinonic acid (MW 200), and related isomers from the oxidation of Δ^3-carene: at *m*/*z* 183, *cis*-pinonic acid [retention time (RT) 23.3 min], and caronic acid (RT 23.9 min); at *m*/*z* 185, *cis*-pinic acid (RT 22.3 min) and caric acid (RT 23.2 min); and at *m*/*z* 199, 10-hydroxypinonic acid (RT 20.7 min) (e.g., Refs. [1, 6, 7, 11–13, 26, 40, 41]). With regard to the

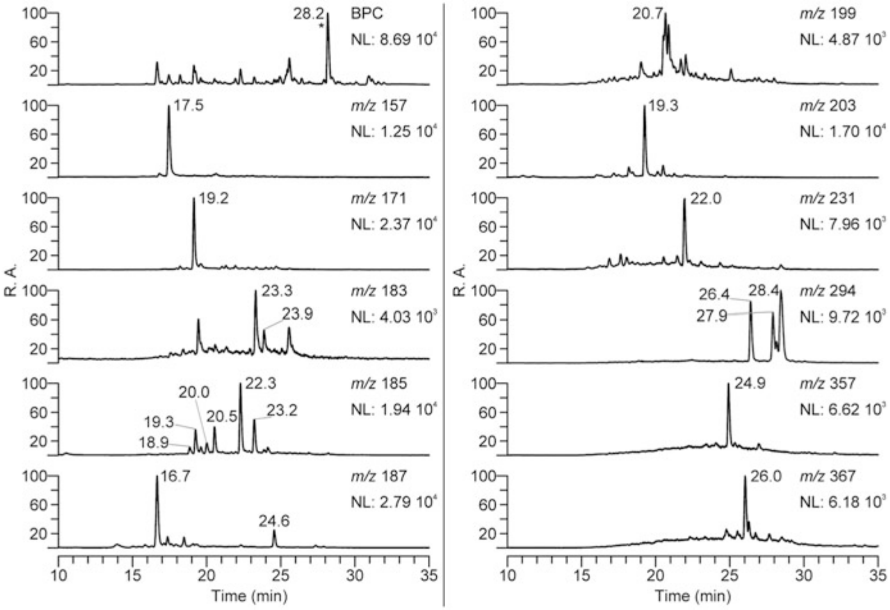

Fig. 18.1 Selected LC/(-)ESI-MS chromatographic data [base peak chromatogram (BPC) and extracted ion chromatograms (EICs)] for a methanolic extract of K-puszta PM2.5 aerosol, containing fresh and aged biogenic SOA. The peak denoted with an *asterisk* in the BPC was also present in the field blank. Abbreviation: *NL* normalisation level (in arbitrary units)

m/*z* 199 compounds, it can be seen that there are additional isomers eluting close to 10-hydroxypinonic acid (RT 20.7 min); these isomers remain to be elucidated.

2. lactone-containing terpenoic acids, terebic (MW 158) and terpenylic acid (MW 172), both α-pinene SOA tracers, and a homologue, homoterpenylic acid (MW 186) from the oxidation of β-pinene: at *m*/*z* 157, terebic acid (RT 17.5 min); at *m*/*z* 171, terpenylic acid (RT 19.2 min); and at *m*/*z* 185, homoterpenylic acid (RT 20.5 min) [3, 38].
3. a C_8-tricarboxylic acid (MW 204), a tracer for aged α-pinene SOA: at *m*/*z* 185 and 203: MBTCA (RT 19.3 min) [36].
4. a still unknown α-pinene SOA tracer: at *m*/*z* 187, tentatively characterised as a C_8-hydroxydicarboxylic acid (RT 16.7 min) [39].
5. diaterpenylic acid acetate, a 1,8-cineole and α-pinene SOA tracer: at *m*/*z* 231 (RT 22.0 min) [3, 16].
6. pinanediol-related MW 295 nitrooxy organosulfates: at *m*/*z* 294 (RTs 26.4, 27.9, and 28.4 min) [8, 15, 21, 34].
7. di-esters formed between pinic acid and a hydroxyl-containing terpenoic acid: at *m*/*z* 357 (RT 24.9 min, hydroxyl-containing terpenoic acid = diaterpenylic acid) [4, 38]; and at *m*/*z* 367 (RT 26.0 min, hydroxyl-containing terpenoic acid = 10-hydroxypinonic acid) [28].

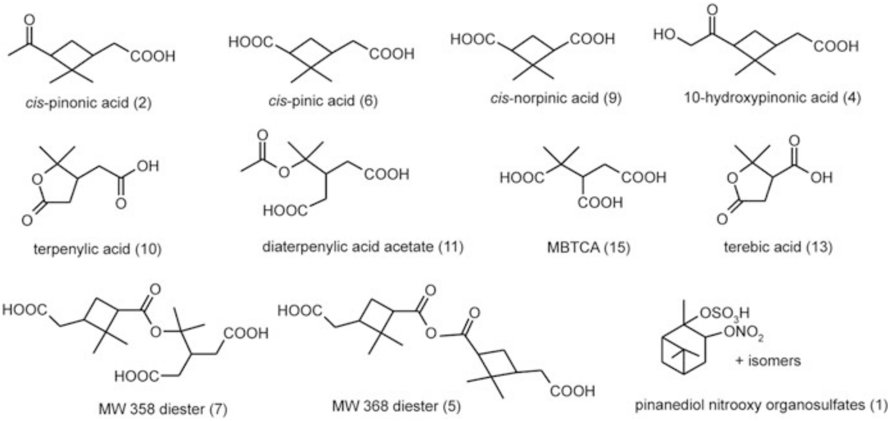

Fig. 18.2 Chemical structures of α-pinene SOA tracers. The numbers between *parentheses* refer to the numbers used in Fig. 18.4

Additional information on the *m*/*z* 185 compounds with RTs 18.9 and 19.6 min, identified as ketolimononic and limonic acids, respectively, and the *m*/*z* 187 compound with RT 24.6 min, identified as the C_9-dicarboxylic acid azelaic acid, can be found in Yasmeen et al. [39].

The chemical structures of the α-pinene SOA tracers that are mentioned above and can be readily detected using LC/(−)ESI-MS is given in Fig. 18.2. These α-pinene SOA tracers should not be regarded as complete; additional minor tracers, for example, are the di-ester formed between *cis*-pinic acid and diaterebic acid [38], and the organosulfates derived from 3-hydroxyglutaric acid and 10-hydroxypinonic acid [34].

Compared to previous work that resorted to GC/MS with prior trimethylsilylation (e.g., Ref. [20]), the number of biogenic SOA tracers that can be readily detected using LC/(−)ESI-MS has increased; a possible reason for this increase is that some of the tracers are not stable (e.g., esters) during the trimethylsilylation procedure and are detected as the corresponding monomers. In addition, some of the organic species such as the lactone-containing terpenoic acids have escaped detected by GC/MS with prior trimethylsilylation.

The tracers listed above, except 10-hydroxypinonic acid and the di-esters, were measured in PM2.5 aerosols that were collected during a 2007 summer campaign at Brasschaat, Belgium, a forest site that is severely impacted by urban pollution [9]. This study showed that the highest atmospheric concentrations of MBTCA and the lowest ones of *cis*-pinonic acid were found during the first five days of the campaign that were characterised by maximum temperatures >22 °C. This is consistent with MBTCA being a tracer for aged biogenic SOA and *cis*-pinonic acid serving as its intermediate precursor. In addition, the unknown MW 188 ($C_8H_{12}O_5$) terpenoic acid revealed the same time series as MBTCA, suggesting that it is also a potential tracer for aged biogenic SOA. Some of the tracers reflected day-time oxidation

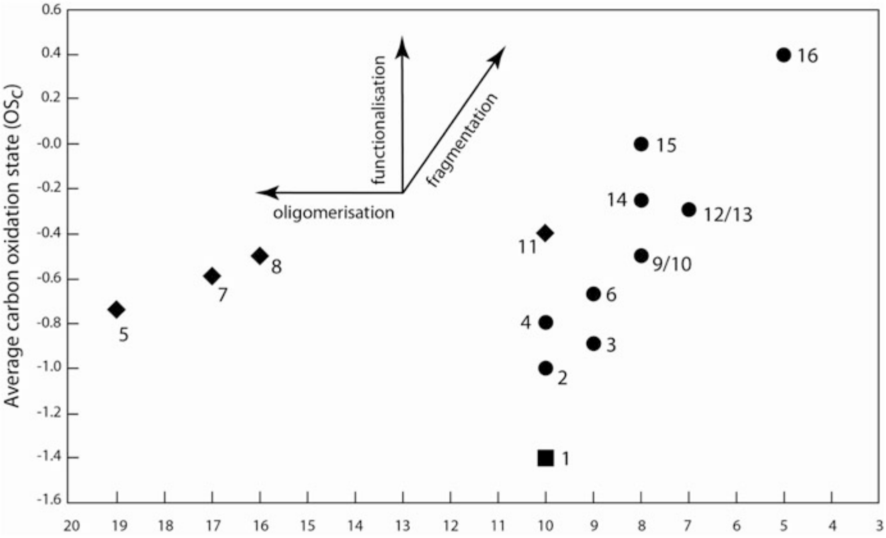

Fig. 18.3 Location of known, recently elucidated, and still unknown α-pinene SOA tracers in the average oxidation framework, developed by Kroll et al. [23]. The di-esters are denoted with ◆, the terpenoic acids with ●, and the pinanediol nitrooxy organosulfates with ■. Note that 3-hydroxy-2,2-dimethylglutaric acid (*11*), terebic acid (*12*), the unknown MW 188 compound (*13*), MBTCA (*14*) and 3-hydroxyglutaric acid (*15*) are located in the *upper right corner*, consistent with tracers for aged α-pinene SOA. *1* pinanediol (nitrooxy organosulfates), *2* pinonic acid, *3* norpinonic acid, *4* hydroxypinonic acid, *5* pinic acid/hydroxypinonic acid, *6* pinic acid, *7* pinic acid/diaterpenylic acid, *8* pinic acid/diaterebic acid, *9* norpinic acid, *10* terpenylic acid, *11* diaterpenylic acid acetate, *12* 3-hydroxy-2,2-dimethylglutaric acid, *13* terebic acid, *14* unknown MW 188, *15* MBTCA, *16* 3-hydroxyglutaric acid

processes (e.g., *cis*-pinonic, terpenylic, and terebic acids, MBTCA, and diaterpenylic acid acetate), while others pointed to night-time aerosol formation processes (e.g., *cis*-pinic, caric, and limonic acids, and the pinanediol-related MW 295 nitrooxy organosulfates). Furthermore, it could be confirmed that MBTCA, in contrast to *cis*-pinonic acid, shows a strong Arrhenius-type temperature relationship, as first documented in a German field study by Zhang et al. [42].

In order to describe the processes of α-pinene SOA formation, which are very complex and dynamic, a useful framework has recently been proposed by Kroll et al. [23]. In this system, the aerosol is presented in terms of the average carbon oxidation state [$OS_C \approx 2(O:C)–H:C$], a quantity that increases with oxidation and is readily measured by a technique such as high-resolution MS (e.g., Refs. [30–32]). As the SOA evolves, it will functionalise, fragment, or oligomerise, with the first two processes affecting the oxidation state. Figure 18.3 places the α-pinene SOA tracers, mentioned above, as well as some additional ones that were reported in the literature, in the average oxidation framework. The latter tracers include norpinonic acid (e.g., Ref. [17]), norpinic acid (e.g., Ref. [6]), 3-hydroxyglutaric acid [2], and 3-hydroxy-2,2-dimethylglutaric acid [2].

18.3 Historic Account on the Discovery of MBTCA: A Search with Failures

The structure elucidation of MBTCA presented an analytical challenge, mainly because the dimethylcyclobutane ring of α-pinene was not retained during its formation. Two approaches can be taken when dealing with the structural elucidation of unknown compounds. A first approach is to isolate the unknown compound in pure form and sufficient quantity, and to elucidate its structure using NMR techniques. A second approach is to synthesise the proposed compound and to compare the chromatographic and mass spectrometric behaviours of the unknown compound with those of the synthesised one. As the first approach was not feasible in the case of a very complex mixture such as α-pinene SOA, the second approach was finally followed.

Our research dealing with MBTCA goes back to 1998, about 2 years before we published an article on "Carbonaceous aerosol characterization in the Amazon basin, Brazil: novel dicarboxylic acids and related compounds" [24]. In the latter study, we focused on the structural characterisation of unknown organic acids that were present in aerosols collected from the Amazon basin, Brazil, during the wet season, and, therefore, were most likely from biogenic origin and not due to biomass burning (taking place in the dry season). These organic acids were found to be enriched in the fine size fraction, suggesting that they were biogenic SOA products formed by gas-to-particle conversion. For the characterisation and structure elucidation of the unknowns, we employed fractionation by solid-phase extraction of the dichloromethane extracts, various types of derivatisations in combination with gas chromatography/mass spectrometry (GC/MS), and detailed interpretation of the electron ionisation (EI) mass spectra. Among the unknowns, a C_8-tricarboxylic acid was identified as 3-carboxyheptanedioic acid (MW 204). However, this identification was tentative since an authentic compound was not available and the identification was only based on the interpretation of mass spectral data. It later turned out that the unknown MW 204 compound was a branched isomer of 3-carboxyheptanedioic acid, i.e., MBTCA. The biogenic precursor of the novel identified compound could not be pinpointed at that time, but we hypothesised that it was most likely a monoterpene or an unsaturated fatty acid. Incidently, the BVOC precursor for the unknown C_8-tricarboxylic acid was later established as the monoterpene α-pinene [18]. A reference compound was still not available, implying that the identification as 3-carboxyheptanedioic acid was still tentative. In a subsequent study [2], the latter structure was questioned because the linear structure of 3-carboxyheptanedioic acid could not be linked to α-pinene, an alternative structure was proposed, i.e., 2-hydroxy-4-isopropyladipic acid, and the proposed compound was synthesised. The EI mass spectral behaviour of its ethyl ester trimethylsilyl ether derivative matched rather well but not completely with that of the unknown MW 204 compound. Its chromatographic retention time deviated slightly from that of the unknown compound, leading to the conclusion that the synthesised compound was likely a diastereoisomer, which, unfortunately, still turned out not to be the right structure. Accurate mass measurements using high-resolution (−)ESI-MS revealed an elemental composition of $C_8H_{11}O_6$ for the deprotonated molecule of the MW 204 a-pinene SOA tracer, which finally led us to revise the structure as MBTCA [36]. A synthetic effort was undertaken by synthesising the proposed compounds, i.e., MBTCA and another positional isomer (i.e., 2-methyl-4-carboxyadipic acid), which were analysed using GC/MS with prior trimethylsilylation and with LC/(−)ESI-MS. The unknown MW 204 α-pinene SOA tracer was unambiguously elucidated as MBTCA because its chromatographic and mass spectral behaviours perfectly agreed with those of the synthesised compound. In this study, *cis*-pinonic acid was proposed as a gas-phase intermediate in the OH radical-initiated formation of MBTCA, a hypothesis which was recently confirmed in an environmental chamber study [29].

18.4 Formation Pathway of MBTCA and Related α-Pinene SOA Tracers

With regard to formation pathways, a route starting with hydrogen abstraction at the C-10 position (relating to the pinane structure [25]) was proposed by Szmigielski et al. [36], while several additional routes were formulated by Müller et al. [29] taking into account that hydrogen abstraction by the OH radical preferentially occurs at certain positions, i.e., the C-1 and C-7 positions [37]. It has to be kept in mind that mechanisms are always to some extent speculative and hard to proof experimentally, and that the initial site where the radical is created due to hydrogen abstraction by the OH radical may migrate. In this regard, evidence has been obtained for the migration of the initial radical site upon OH radical-initiated oxidation of α-pinene in the presence of NO and highly acidic sulfuric acid-containing seed particles; more specifically, upon formation of the MW 295 nitrooxy organosulfates the initial radical site on the cyclohexane ring migrates to a ring position and the methyl group of the dimethylcyclobutane ring [34]. Figure 18.4 proposes a revised mechanistic route to MBTCA starting with hydrogen abstraction at the favoured C-4 position (C-2 position of *cis*-pinonic acid). As in the case of the initial OH radical attack on *cis*-pinonic acid, the attack of an OH radical on intermediate (d) may proceed through an initial attack at another carbon atom. It can be noted that the formation of MBTCA starting from *cis*-pinonic acid requires two molar OH radical equivalents.

The route proposed in Fig. 18.4 has the merit that it also allows one to explain the formation of several other known and more recently elucidated α-pinene SOA tracers, i.e., *cis*-pinic acid (e.g., Refs. [7, 41]), 10-hydroxypinonic acid [6, 40], 3-hydroxyglutaric acid [2], and 3-hydroxy-2,2-dimethylglutaric acid [2] (Fig. 18.5).

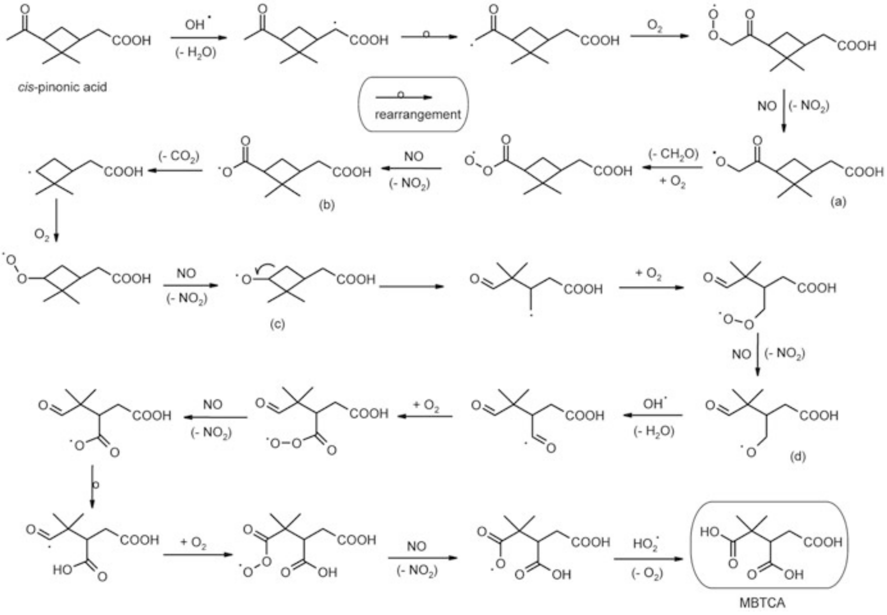

Fig. 18.4 Proposed revised mechanistic pathway leading to MBTCA

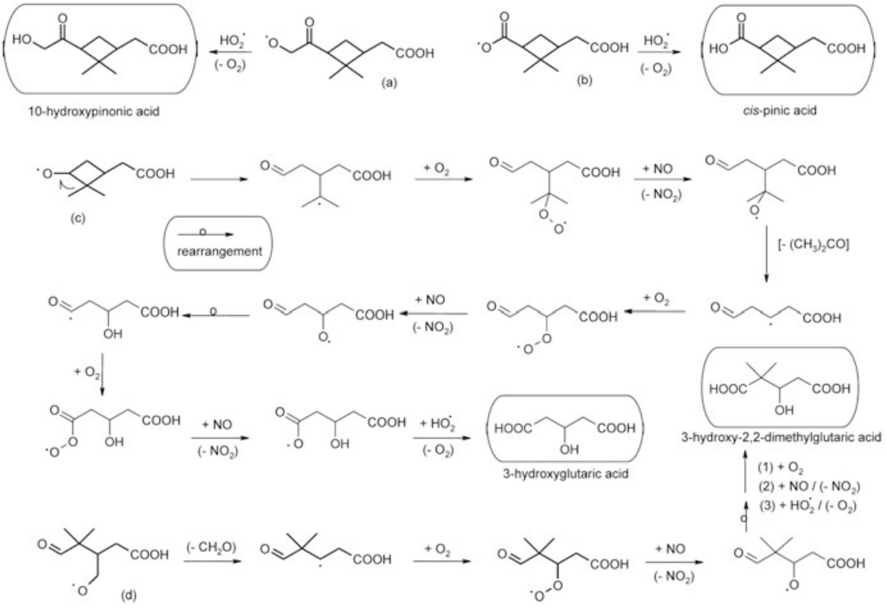

Fig. 18.5 Proposed revised mechanistic pathway leading to known and recently elucidated α-pinene SOA tracers, i.e., *cis*-pinic, 10-hydroxypinic, 3-hydroxyglutaric, and 3-hydroxy-2,2-dimethylglutaric acids. For the route leading to intermediates (*a*–*d*), see Fig. 18.4

18.5 Conclusions and Perspectives

Significant progress has been made during the last decade with the structural characterisation of α-pinene and related monoterpene (i.e., β-pinene, *d*-limonene, and Δ^3-carene) SOA tracers. Hence, we have now reached the stage where the major terpenoids in ambient fine forest aerosol that is enriched in biogenic SOA have been identified. A major terpenoic acid from the photo-oxidation of α-pinene, however, which shows a high relative abundance in ambient fine forest aerosol but remains to be fully identified, is the $C_8H_{12}O_5$ hydroxydicarboxylic acid. Since it is a potential tracer for aged biogenic SOA, its structural elucidation would be warranted. Another class of SOA tracers that have only been partially explored and for which suitable analytical methods still have to be developed are the organosulfates. These tracers have a mixed biogenic/anthropogenic origin since their formation involves the participation of sulfuric acid which is of anthropogenic origin. Furthermore, more detailed insights are required on the time evolution of oxygenated and processed (e.g., esterified) products during laboratory irradiation experiments under simulated atmospheric conditions to better constrain their suitability as tracers for photochemical and other ageing processes.

Characterisation of α-pinene and related monoterpene SOA tracers at the molecular level using a chromatographic technique (GC or LC) hyphenated to a mass spectrometric technique and detailed interpretation of MS fragmentation data can be analytically challenging, as was the case for MBTCA which had not retained the dimethylcyclobutane ring of α-pinene. It was a search with several failures in which we experienced that nature does not reveal its secrets all at once. However, it was worth the efforts since it resulted in the structural elucidation of a major tracer for aged biogenic SOA that is useful for ambient fine aerosol characterisation.

An emerging analytical technique for the detailed characterisation of biogenic SOA, including minor components, is high-resolution MS such as Fourier Transform Ion Cyclotron Resonance MS (FT-ICR MS). This technique enables the accurate measurement of the numerous molecular masses present in a complex SOA mixture and as such their O:C ratio (and their average carbon oxidation state) which increases upon photochemical ageing. It allows for a detailed characterisation of biogenic SOA that is complementary to that achieved with GC- or LC-based MS techniques and interpretation of MS fragmentation data.

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