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A rapid method for the analysis of methyl dihydrojasmonate and galaxolide in indoor and outdoor air particulate matter☆

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ABSTRACT

A method for the analysis of methyl dihydrojasmonate (MHDJ) in air particulate matter (PM_1 and $PM_{2.5}$) is described for the first time. This fragrance is determined together galaxolide (HHCB). Airborne particles were collected by filtration of air volumes between 100 and 1000 m^3. Recovery efficiencies of filter extraction with Soxhlet and pressurized liquids were evaluated. The method included reaction with BSTFA:TMCS for generation of trimethylsilyloxy derivatives which prevented deleterious effects in the gas capillary column by interaction of hydroxyl groups from air constituents other than these fragrances. This step avoided the use of additional clean up methods such as liquid column chromatography affording direct quantification by GC-EI-MS. The proposed method had enough sensitivity for quantification of these fragrances in indoor and outdoor environmental samples using small aliquots of the PM extracts, e.g. 2.5%, and therefore saving sample material for eventual determination of other compounds. The detection limits were 0.03 ng and 0.01 ng for MHDJ and HHCB, respectively.

Both MHDJ and HHCB were predominantly found in the smallest PM fraction analyzed (<0.5 μm). The outdoor concentrations were highest in busy urban streets. However, indoor levels in school classrooms and subway stations were one order of magnitude higher than those observed outdoor. This difference was consistent with the use of these compounds as additives in cleaning and personal care products and the small dispersion of these fragrances in indoor environments. Information on the occurrence of this and other fragrances is needed to increase the understanding on the influence of anthropogenic activities in the formation of organic aerosols and source apportionment.

1. Introduction

Urban atmospheres contain a complex mixture of organic compounds from natural and anthropogenic sources. Methyl dihydrojasmonate (MDHJ) is an additive in cleaning and personal care products used in a wide range of products. This compound and other synthetic fragrances, e.g. galaxolide (HHCB), are semivolatile (Table SI1) and therefore incorporated to the ambient air after use. There is a need to know what is the role of this compound in the atmosphere, namely in urban areas where population density is highest. However, no analytical method for MDHJ had been described so far. Furthermore, the number of studies considering the occurrence of fragrances in atmospheric environments is relatively small in view of their widespread use [1]. MDHJ is a cyclopentenone (Table SI1) [2] of potential aphrodisiac properties that is used in perfumes and flavors [3,4]. It is an ingredient for base and middle notes in perfumery because it remembers jasmine odor [4]. HHCB is lipophilic (Table SI1), has a musk-like odor and is an additive in cosmetics, perfumes, cleaning, polishing and washing agents, household products and aromatic oils. In view of this large number of applications this compound is in the EPA list of Protection Volume [5,6]. It accumulates in the adipose tissue and has been detected in wildlife and humans, including breast milk [7]. It is also a suspect endocrine disruptor for possible estrogenic and androgenic effects [7].

MDHJ and HHCB have been found in residual waters [8–13], biota and sediments [1,10,14]. No reports are available for the occurrence of MDHJ in air and the number of studies on the occurrence of HHCB in outdoor ambient air is limited [9,15–18] and mainly focused on potential emission sources and degradation products. Due to their semi-volatility, these compounds high

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relative high particle binding affinity involving adsorption onto ambient air particulate matter (PM) which could be especially relevant in indoor environments. Adults and children spend large part of their time indoors, where the air could be more contaminated than outdoors [17,19–22]. Besides buildings, the public transport systems, such as the subway, are also important indoor environments for daily exposure in modern urban areas [23]. Moreover, HHCB has been found in house hold cleaning products and was detected in the ambient air PM in various indoor environments, including kindergartens [21,24–26]. All these antecedents outline the need for rapid methods for the analysis of these compounds in air particles.

Previous analytical methods involved air filtration, filter extraction and liquid chromatographic clean up [15,20]. In the present study, a method to determine the concentrations of MDHJ and HHCB in ambient air PM of urban environments has been developed. Soxhlet and pressurized liquid extraction (PLE) were tested for the analysis of filter samples. Bis-(trimethylsilyl)-trifluoroacetamide and trimethylchlorosilane (BSTFA:TMCS, 99:1) and pyridine were added to the sample extracts to obtain the corresponding trimethylsilyl (TMS) ether or ester derivatives. The studied synthetic fragrances do not contain free hydroxyl groups (Table SI1) and are analyzed underivatized. However, the above derivation step is needed to elute air constituents containing hydroxyl groups through the gas capillary column. The derivatization procedure eliminates a large number of compounds which would interfere in the performance of the chromatographic column and at the same time allows to analyzing other organic compounds, such as saccharides and acids, in a single run by gas chromatography coupled to mass spectrometry (GC–MS) [27].

Samples were collected between 2012 and 2013 in Barcelona, one of the most densely populated European urban areas. They include an urban background site, a busy road site and roof site, in- and outdoor air PM from two primary schools, and indoor air collected at four subway station platforms.

2. Experimental

2.1. Reagents and analytical standards

High purity dichloromethane (DCM) and methanol (MeOH) were used for extraction (UniSolv® and SupraSolv®, respectively; Merck KGaA, Darmstadt, Germany).

BSTFA:TMCS (99:1) were from Supelco (Bellefonte, PA, USA). Pyridine was from Fluka Analytical (Steinheim, Germany).

The standards were of the highest commercially available purity (>85 %): MDHJ (mixture of *cis* and *trans*) and 1-phenyldodecane were purchased at Fluka Analytical (Steinheim, Germany). HHCB were supplied by Sigma Aldrich (Steinheim, Germany). d_7-Levoglucosan was from Cambridge Isotope Laboratories (Andover, MA, USA). Stock individual solutions were stored at −20 °C, while BSTFA and pyridine reagents were stored at 4 °C.

2.2. Sampling

Outdoor sampling in the urban background of Barcelona was performed with a six stage Anderson cascade impactor to collect atmospheric particles of different sizes (>7.2; 7.2–3; 3-1.5; 1.5–1; 1–0.5; <0.5 μm) using a high volume (HiVol) sampler (MCV). Samples involving filtration during 72 h were obtained with glass fiber filters (Whatman, Maidstone, UK) [28]. Another outdoor sampling of PM_1 (aerodynamic particle diameter lower than 1 μm) was conducted in two urban sites in Barcelona at street level and at a roof 40 m above the street level using a Digitel-DH80HiVol sampler (Digitel Elektronic AG, Switzerland) that was equipped with a 150 mm diameter quartz filter (2500QAT-UP; Pallflex, Pall Corporation). Each filter encompassed 12 h sampling time during cold and warm periods [29]. In schools, $PM_{2.5}$ samples (aerodynamic particle diameter lower than 2.5 μm) were obtained using a HiVol sampler (MCV) equipped with a quartz fiber filter (2500QAT-UP). PM was collected from Monday to Friday at an 8 h sampling resolution during school activity. This sampling was performed simultaneously in classrooms with pupils and in the playground (outdoors) [30]. In the subway, PM was sampled in four different stations during cold and

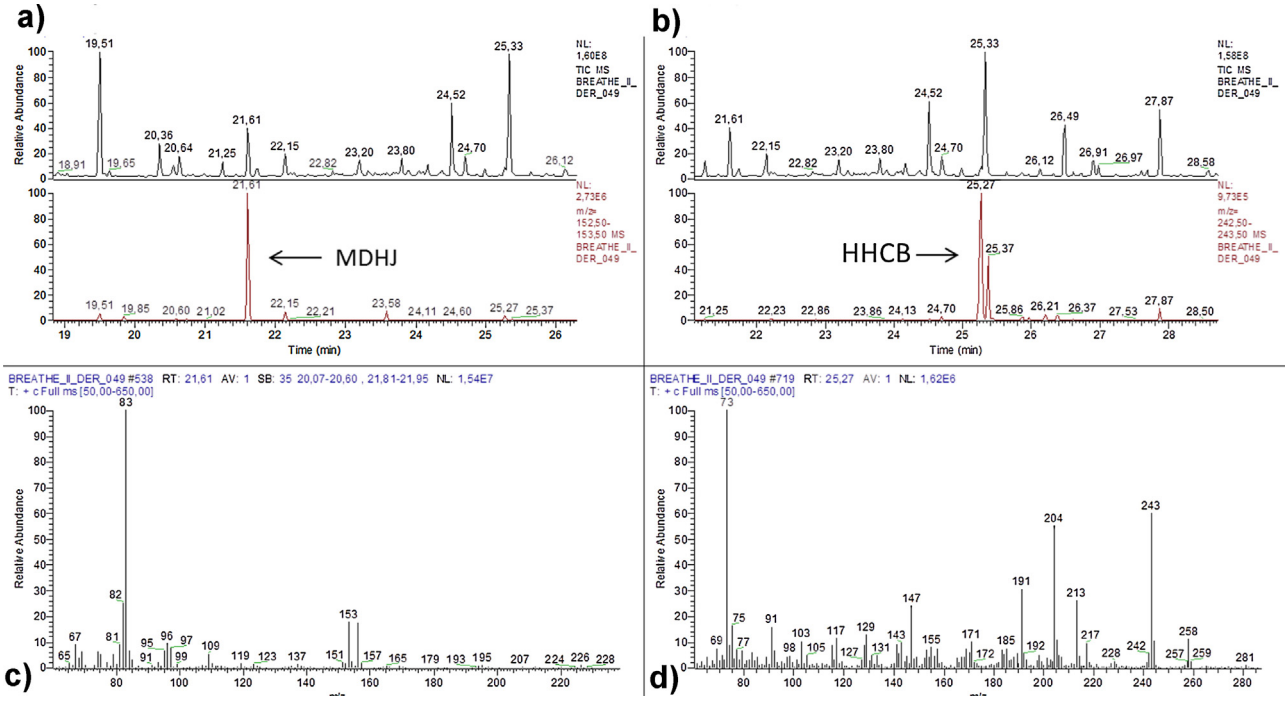

Fig. 1. Full scan of urban street PM_1 extract, mass fragmentograms and mass spectra of MDHJ (a, *m*/*z* 153; c) and HHCB (b, *m*/*z* 243; d).