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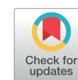
Composition and authentication of commercial and home-made white truffle-flavored oils



Florian Wernig [a], Franz Buegger [b], Karin Pritsch [b], Richard Splivallo [a, *]

[a] Institute for Molecular Biosciences, Goethe University Frankfurt, Frankfurt am Main, Germany
[b] Institute of Biochemical Plant Pathology, Helmholtz Zentrum München, German Research Center for Environmental Health, Neuherberg, Germany

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ABSTRACT

Truffle-flavored olive oils sell at a high premium compared to unflavored oils, yet, their rarely contain either real truffles or natural truffle aroma. Our aim here was to characterize truffle oils and explore techniques for authentication. Specifically, we characterized and compared by metabolic profiling and stable isotope ratio analysis the flavors emitted by commercial and home-made truffle-flavored oils (prepared with natural and synthetic flavors), non-flavored oils, and actual fruiting bodies of the white truffle *Tuber magnatum*.

Stable isotope ratio analysis ($\delta^{13}C$) of 2,4-dithiapentane, a characteristic truffle odorant detected in most flavored oil samples, could not differentiate between natural and synthetic flavors. By contrast, metabolic profiling revealed that truffle flavor was imprinted to oils by four to six sulfur containing volatiles, two of which (dimethyl sulfoxide and dimethyl sulfone) were exclusively detected in commercial oils, regardless of their synthetic or natural labeling. Overall our results also highlight inconsistencies in product labelling and question the authenticity of oils claiming to contain only natural truffle flavors.

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1. Introduction

With thousands of euros per kilograms, truffle fungi (*Tuber* spp.) stand among the most expensive food items on our planet. This luxury status can be traced back to truffle's enticing aromas, which partially originate from intimate interactions between the fungus and its microbiome (Splivallo & Ebeler, 2015; Splivallo et al., 2014). Human sensed aroma of any food can typically be attributed to a blend of 3–40 odorants (Dunkel et al., 2014), and truffle are no exception. Indeed, the aroma of white and black truffles is made of 10–20 odorants per species (Culleré et al., 2010; Liu, Li, Li, & Tang, 2012; Schmidberger & Schieberle, 2017; Splivallo & Ebeler, 2015).

Once harvested, truffle fruiting bodies quickly degrade and can be stored fresh for up to ten days (Splivallo & Culleré, 2016). Similarly, derived products prepared from fresh truffles (*i.e.* truffle cheese, truffle-flavored oil) suffer from a short shelf-life and are only available during the truffle season which typically lasts a few months in a year. To circumvent the latter shortcomings, the food industry has for long relied on synthetic flavors (i.e. odorants) for impairing truffle flavor to food (Splivallo, Ottonello, Mello, & Karlovsky, 2011). The exact composition of truffle flavors used by the food industry is unknown, even if truffle flavored-oils are said to contain more than 60 volatiles, of which 2,4-dithiapenatne is the most typical one (Pacioni, Cerretani, Procida, & Cichelli, 2014; Torregiani et al., 2017). Indeed, 2,4-dithiapentane, has a characteristic white truffle smell, and occurs in the white truffle *T. magnatum* (Splivallo et al., 2011) but also in the garlic mushroom *Marasmius alliaceus* (Rapior, Breheret, Talou, & Bessière, 1997) and in boiled carp fillets (*Cyprinus carpio L.*) (Schlüter, Steinhart, Schwarz, & Kirchgessner, 1999) and in numerous microbes (Lemfack, Nickel, Dunkel, Preissner, & Piechulla, 2014). Natural 2,4-dithiapenatne (not originating from truffles) has recently appeared on the market and sells at a large premium compared to its synthetic counterpart. Important price premiums (40–200 times the synthetic (Dubal, Tilkari, Momin, & Borkar, 2008)) are typical for natural flavors, which increases the risk of falsification in food and begs for authentication and traceability methods to be developed (Van Rijswijk & Frewer, 2012).

Two techniques, which have been widely applied by the food industry towards the authentication and traceability of volatile flavors (odorants), are gas-chromatography-mass spectrometry

* Corresponding author.
E-mail address: richard.splivallo@a3.epfl.ch (R. Splivallo).

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(GC-MS) and GC-isotope ratio mass analysis (GC-IRMS). For instance, a study by GC-MS exemplified that specific volatile markers can reveal the geographical origin of honey and the identity of the botanicals that were collected by honeybees to make that honey (Radovic et al., 2001). GC-IRMS is another valuable technique for flavor authentication. It relies on the fact that the isotopic ratio of certain elements (i.e. hydrogen, carbon, nitrogen, oxygen, sulfur) can provide, similarly to a fingerprint, information about the origin of some flavors (i.e. geographical origin or a natural vs. synthetic sources) (van Leeuwen, Prenzler, Ryan, & Camin, 2014). In the food industry, authenticity studies by GC-IRMS have been used for fruits, essential and edible oils, fats, beverages and vinegars (van Leeuwen et al., 2014). The technique has also been successfully applied to distinguish synthetic from natural vanillin or strawberry and cinnamon flavors (Hansen, Fromberg, & Frandsen, 2014; Schipilliti, Dugo, Bonaccorsi, & Mondello, 2011; Sewenig, Hener, & Mosandl, 2003).

The aim of our study was to shed light on the differences among commercial and home-made white truffle oils using the analytical techniques mentioned in the previous paragraph. Our motivation was fueled by the recent appearance on the market of white truffle oils claiming to contain “natural truffle” aromas. In short, the volatile profiles of regular olive oils and truffle-flavored oils (commercial and home-made) were investigated by untargeted metabolic profiling using GC-MS. GC-IRMS was further employed to assess whether the carbon isotopic ratio of 2,4-dithiapentane, the major odorant identified in our truffle-flavored oils, could be further used to discriminate among natural and synthetic aromas?

2. Materials and methods

2.1. Oil and truffle samples

Five regular (non-flavored) and ten truffle-flavored olive oils were purchased online or from supermarkets and grocery stores in Germany and Switzerland. The olive oil of most samples originated from Italy as highlighted in Table 1. Four of the truffle-flavored oils were labelled as containing “natural truffle aroma” while the remaining six contained synthetic flavors (Table 1). Fruiting bodies of *T. magnatum* were used either fresh or after being stored frozen at -20 °C (Table 1). Home-made truffle oils were prepared by extracting 50, 100 or 200 mg ml^{-1} of crushed *T. magnatum* fruiting bodies (from Serbia, see Table 1) in oil C1 for 24 h (300 rpm). Species identification of *T. magnatum* fruiting bodies was confirmed by the morphological characteristics of truffle spores.

2.2. Untargeted metabolic profiling of oils by GC-MS

Sixteen oils from Table 1 (marked “VOC” in the experiment column) were analyzed in triplicates by untargeted metabolic profiling to identify volatile markers that could discriminate specific group of samples (i.e. natural vs. synthetic, home-made vs. commercial). Oil samples of 1 ml were enclosed in 20 ml vials equipped with PTFE septa and analyzed by GC-MS. Volatiles were collected from the headspace of the vials by a pressure balanced headspace trap (TurboMatrix Air Monitoring Trap from Perkin Elmer – filled with activated charcoal beads) by an auto sampler (Perkin Elmer, Headspace Sampler TurboMatrix 40) under the following conditions: vials were heated for 20 min at 80 °C and volatiles were trapped at 30 °C after piercing the membrane of the vial. This system is equivalent to a cartridge packed with adsorbing material operated in purge and trap mode. An internal standard (4-fluorobromobenzene, 100 µl of a 27.2 Internal standard (IS): N2 (µmol/mol)) was injected into the vials prior to volatile sampling. Volatiles were released of the trap by thermal desorption at 280 °C and separated by the gas chromatograph (Perkin Elmer, Clarus 680) equipped with a capillary column Elite-5MS (Ø 0.25 mm; length 30 m; film thickness 1.00 µm). The following method was used for volatile separation: run time: 52.33 min, start at 30 °C and hold for 5 min; ramp at 03 °C min^{-1} to 160 °C; ramp at 50 °C min^{-1} to 260 °C hold for 2 min. Helium was used as carrier gas with constant pressure at 75 kPa. Masses were detected by a quadrupole detector of the mass spectrometer (Perkin Elmer, Clarus SQ8 C). Volatiles were ionized by electron impact at -70eV and detected by the quadrupole in scan mode (m/z 50–300).

2.3. Data processing of volatile profiles

Full volatiles profiles were processed for peak-realignment by TagFinder 4.1 (Luedemann, Strassburg, Erban, & Kopka, 2008). Specifically, chromatograms were converted to CDF-files and the tool “PeakFinder” of the software TagFinder 4.1 was run with the following parameters: Smooth Width Apex Finder = 1, Smooth Width ± Apex Scan = 1, Max Merging Time Width = 1.0, Time Scan Width = 4.0. Check marks in Large File Mode and Scan for TAGs were also activated. Low Intensity Threshold was set to 2,000,000. TagFinder generates a data matrix of TAGs as output files, where each TAG represents one detected mass within a retention time range. Background noise was removed by subtracting TAGs from an empty 20 ml vial containing no samples. The nonparametric Kruskal-Wallis test was applied to identify volatiles markers that differed in intensity among oil samples ($p \leq 0.05$ in R (R Core Team., 2014)).

2.4. Volatile identification

Volatiles were analyzed by GC-MS and their MS fragmentation patterns were compared with entries in the National Institute of Standards and Technology (NIST 2011) library v2.0. Kovats indices, computed after injection of an alkane standard (C8 to C30, Sigma-Aldrich), were compared to literature values available in the NIST library and in the Pherobase database (www.pherobase.com). Compound identification was furthermore confirmed by injection of synthetic standards purchased from Sigma-Aldrich for the following volatiles: 2-butanone, dimethyl sulfide (DMS), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS), dimethyl sulfoxide (DMSO), 2,4-dithiapentane (syn: bis(methylthio)methane), hexyl acetate, 2-methylbutanal, 3-methylbutanal, 3-methyl-1-butanol, 2-methyl-1-propanol, 1-octen-3-ol and 2-phenylethanol.

2.5. Concentration determination of sulfur containing compounds

Quantification of volatiles was performed with the cartridge used in purge and trap mode as highlighted under section 2.2 (TurboMatrix Air Monitoring Trap from Perkin Elmer). Concentrations of sulfur containing compounds were determined by external calibration curves using dilutions of authentic standards made in olive oil. Calibration curves were based on at least four different concentrations. Peak areas (PA) for each compound were computed for specific mass fragments (m/z): DMS: m/z 62; DMDS: m/z 94; DMTS: m/z 126; 2,4-dithiapentane: m/z 108 and quantification was performed based on the ratio of the peak area of the analyte to the peak area of the internal standard (4-fluorobromobenzene; m/z 174).

2.6. Isotope ratio mass analysis of 2,4-dithiapentane

Stable isotope ratio ($\delta^{13}C$) analyses were performed for truffle-flavored oils (Table 1), *T. magnatum* fruiting bodies (Table 1) and four synthetic 2,4-dithiapentane samples (two vials purchased

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