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The cooked shellfish-odour of the mushroom *Russula xerampelina*

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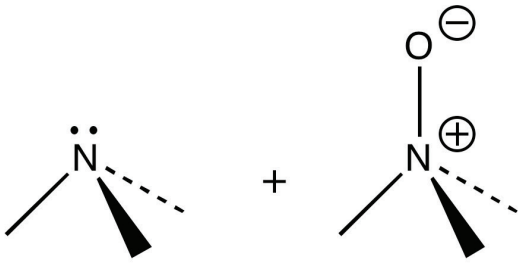
Abstract

The "shrimp mushroom", *Russula xerampelina,* has a strong cooked shellfish odour. Headspace volatiles from fresh sporocarps of this mushroom were analysed using solid phase microextraction (SPME) and gas chromatography–mass spectrometry (GC–MS). Trimethylamine and trimethylamine *N*-oxide were the only volatile compounds detected emanating from the fruiting body. Trimethylamine is noted for its fishy, cooked crab or cooked shrimp-like odour.

Graphical Abstract



Key Words

GC-MS, *Russula xerampelina* (Agaricales; Russulaceae), Shrimp Mushroom, SPME, Trimethylamine, Trimethylamine *N*-oxide

Introduction

Mushrooms have a wide variety of odours, which are key characters in their identification (Gilbert 1932; Chiron and Michelot 2005; Fraatz and Zorn 2010). A fishy, cooked crab or cooked shrimp-like odour has long been noted as part of the field description of a number of mushroom species (Gilbert 1932; Adamčík and Buyck 2011). The most notable mushroom with this odour is the "shrimp mushroom", *Russula xerampelina* (Schaeff.) Fries (Russulaceae, Agaricales). This wild mushroom is edible and is highly prized by mushroom hunters (Kuo et al. 2007). The crustacean-like odour is one of the ways foragers use to identify this mushroom.

Trimethylamine has long been associated with this mushroom's odour. Singer (1926) noted it smelled strongly of trimethylamine (lobster or herring-like). In 1957 von Kamienski found trimethylamine in mushrooms during a study of volatile amines from plants and mushrooms. Trimethylamine was characterized in this study by the distinct "smell of herring". Senatore et al. (1988) thought *R. xerampelina*'s taste was mediocre and that it had the "smell of trimethylamine". Before modern chemical instrumentation, trimethylamine's odour

was used for identification, due to the difficulty in preparing a solid derivative for positive confirmation. Gas chromatography–mass spectrometry (GC–MS) analysis identified trimethylamine and trimethylamine *N*-oxide as volatiles from these mushrooms.

Methods

To investigate the source of this odour, we collected and analysed volatiles from fresh sporocarps of *R. xerampelina* collected in Humboldt County, California (identified by DLL). Voucher specimens (Collection Numbers 3142 and 9933) are in the Cal Poly Humboldt Mycological Collection. Headspace analysis was done by inserting the absorbent tip of a 100 µm polydimethylsiloxane Supelco solid phase microextraction (SPME) apparatus between the gills of *R. xerampelina* for 20 minutes. Immediate analysis by gas chromatography–mass spectrometry (GC-MS) showed only two volatile components were present. Data collection was started on GC injection to identify all highly volatile compounds captured on the SPME filament.

Results and discussion

The two volatile components captured on the SPME apparatus were initially identified as trimethylamine and trimethylamine *N*-oxide by comparison of published mass spectra in the NIST 1998 computerised mass spectral library. Identical mass spectra and retention times were obtained by GC–MS analysis of commercial samples of these compounds. The mass spectra were: trimethylamine [m/z = 60(M^++1, 2), 59(M^+, 47), 58(100), 57(7), 56(4), 44(4), 43(8), 42(29), 41(4), and 40(6)]; and trimethylamine *N*-oxide [m/z = 75(M^+, 20), 59(30), 58(100), 57(7), 56(4), 45(25), 43(13), 42(26), 41(4), and 39(3)].

The chemicals responsible for odours of cooked crab, shrimp or lobsters have been extensively studied (Kubota and Kobayashi 1988; Kubota et al. 1989; Lindsay 1990; Chung and Cadwallader 1994; Cadwallader et al. 1995; Baek and Cadwallader 1997; Ishizaki et al. 2005; Chen and Zhang 2010; Gu et al. 2014; Okabe et al. 2019). Many different odour compounds have been identified as part of cooked crustacean odour profiles. The odour compounds that are described as smelling like cooked shellfish include, ammonia and amines, thiols and sulphides, nitrogen heterocycles, and carbonyl compounds. Some, but not all, of these studies include trimethylamine as part of volatiles identified; none report trimethylamine *N*-oxide. Of the many possible crustacean-like odour compounds identified from cooked shellfish only trimethylamine is present in this mushroom.

To our knowledge this is the first identification of trimethylamine *N*-oxide from mushroom fruiting bodies. This compound degrades to trimethylamine and its odour threshold has been reported to be less than one part per billion (Leonardos et al. 1969). This low odour threshold and decomposition of trimethylamine *N*-oxide would explain why dried specimens of *R. xerampelina* in mycological collections continue to smell of trimethylamine for many years.

It is possible that trimethylamine protects this mushroom's sporocarp from being eaten by fungivores, repel flies and gnats or slugs. In recent field collections (by DAD) fungal gnat maggots were only noted in old and decaying sporocarps. Unlike attraction to the stink horn, *Phallus impuducus*, or rotting animal carcasses, carrion flies have not been observed to swarm on this mushroom (by WFW). We note that trimethylamine being part of the odour of decaying flesh, so this mushroom might be expected to attract these flies.

A number of allomone or allelochemical slug antifeedant chemicals have been studied from mushroom fruiting bodies. A volatile compound frequently produced by mushrooms called "mushroom alcohol", 1-octen-3-ol, is a known slug antifeedant (Wood et al. 2001). Banana slugs, *Ariolimax columbianus* (Gould), stops eating the mushroom, *Clitocybe flaccida*, after an initial bite. Clitolactone, 5-(chloromethyl)-3-methyl-2(5H)-furanone, was isolated from sporocarps of this mushroom and was shown to inhibit feeding behaviour of this slug (Wood et al. 2004). Further studies need to be done to see if trimethylamine or trimethylamine *N*-oxide deters feeding banana slugs.

It is possible that trimethylamine being part of the odour of decaying flesh is an allomone that protects this mushroom's sporocarp from being eaten by mammalian fungivores. In nature this compound is generally produced from plant and animal decomposition. Mushrooms are an important part of the diet of deer and small mammals. This is a way of spore dispersal for some fungal species. Analysis of spores from the digestive tracts of small mammals that eat fungi, find only 1% of the spores detected are from the family Russulaceae (Maser et al. 1978). This difference might arise from antifeedants in these fungi or availability of *Russula* species in the Oregon coniferous forests where this study was done.

In nature, trimethylamine *N*-oxide is an osmolyte found in marine crustaceans and marine fish. This compound acts to stabilize proteins and nucleic acids from distortion due to water pressure and urea concentrations. The freshness of marine animals in the market place is judged by the lack of trimethylamine produced by bacterial decomposition of trimethylamine *N*-oxide.

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