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REVIEW

Mushroom Flavor

Joseph A. Maga

The flavor chemistry of various mushroom species is reviewed with primary emphasis on the volatiles that have been identified in mushrooms. Also considered is the influence of processing and preservation on volatile compound formation and the organoleptic properties associated with the major mushroom volatiles.

Considering that the mushroom is usually consumed for its unique flavor properties, surprisingly few detailed studies have appeared on the flavor chemistry of mushrooms. Interestingly, the few studies that have been published at first appear to be in direct conflict relative to which fraction is primarily responsible for the flavor properties of the mushroom. Certain investigators (Craske and Reuter, 1965) placed major emphasis on the nonvolatile nitrogenous constituents. Specifically they reported that with dried *Boletus edulis*, the highly basic amino acids contributed most to its characteristic flavor. Likewise, Altamura et al. (1967) in working with *Agaricus campestris* reported on the isolation and identification of a series of novel free amino acids which they felt could enter into the characteristic flavor of this mushroom, especially upon heating. In addition, mushrooms have relatively high levels of free glutamic acid (Hac et al., 1949) and numerous potentially reactive carbohydrates (Hughes et al., 1958; Litchfield, 1967; Holtz, 1971) as well as other flavor enhancers (Nakajima et al., 1961) that can also be influential in flavor development during heat processing. Another possible precursor flavor compound source, especially in dried mushrooms, would be the presence of unsaturated fatty acids in certain species (Leegwater et al., 1961, 1962).

In the case of the dried mushroom *Cortinecius berkeleyanus*, Take and Otsuka (1965) reported that quanylic acid was the primary flavor compound. Likewise, enzymatic flavor formation can predominate in certain species (Yasumoto et al., 1976).

In contrast, most recent reports have placed major emphasis on the volatile fraction as being the major contributor to characteristic mushroom flavor. In retrospect, both the early and more recent reports are probably both partially correct, for as in the case for most foods, their sensory properties can rarely be attributed to one specific type or class of compounds. Another major factor to consider in this apparent controversy is the fact that the sensory compounds responsible for mushroom flavor can vary dramatically among species (Abbott and San Antonio, 1974; Dijkstra, 1976; Pyysalo, 1976; Sulkowska and Kaminski, 1977), as well as be influenced by cultural practices (Humfeld, 1948; Humfeld and Sugihara, 1952; Block et al., 1953; Sugihara and Humfeld, 1954; Gilbert, 1960; Moustafa, 1960; Litchfield et al., 1963; Dijkstra et al., 1972). However, the remainder of this review will deal primarily on the role of the volatiles associated with mushrooms since this apparently is the primary flavor compound source for most mushroom species.

LOCATION OF MUSHROOM AROMA

Perhaps a most logical first question would be to ask if typical mushroom aroma is associated with any particular

Colorado State University, Department of Food Science and Nutrition Fort Collins, Colorado 80523.

part of the mushroom. This basic question was investigated in an interesting early study by Bernhard and Simone (1959) using the common raw field mushroom *A. campestris*. They carefully separated the mushroom into the cap, stem, gills, cap cuticle, and stem cuticle and evaluated mushroom odor intensity of equal weights of each portion by means of a paired comparison sensory evaluation. Their data demonstrated no statistically significant difference in aroma intensity between the intact cap and stem and the intact cap and cap cuticle. However, significant differences were noted when the stem and gills, stem and stem cuticle, and the cap and gills were compared. Thus, at least for this species it would appear that there are sensory differences as influenced by mushroom part but from a practical standpoint processors and consumers normally do not "peel" their mushrooms or use only the peel or gill portions. Since the above study only evaluated one species, an expanded similar study involving other species would be of interest. Along these lines, apparently no data have been published attempting to correlate any possible flavor intensity differences as influenced by maturity and/or storage time and conditions after harvest.

VOLATILES IDENTIFIED IN MUSHROOMS

The actual number of different volatile compounds identified in various mushroom species approaches 150 and represents a wide variety of compound classes (Murahashi, 1936, 1938; Morita and Kobayashi, 1966; Wada et al., 1967; Cronin and Ward, 1971; Stauble and Rast, 1971; Picardi and Issenberg, 1973; Thomas, 1973; Kaminski et al., 1974; Wasowicz, 1974; Dijkstra, 1976; Dijkstra and Wiken, 1976a,b; Pyysalo, 1976; Pyysalo and Suihko, 1976; Yasumoto et al., 1976; Card and Avisse, 1977; Pyysalo and Niskanen, 1977; Sulkowska and Kaminski, 1977).

At this point some of the important volatile flavor compounds isolated from mushrooms will be discussed in further detail. Currently, it is generally conceded that a series of compounds containing eight carbons are the primary volatiles contributing to mushroom flavor. Compounds in this class include 1-octanol, 3-octanol, 3-octanone, 1-octen-3-ol, 2-octen-1-ol, and 1-octen-3-one.

Murahashi (1936) isolated the main volatile of the *Tricholoma matsutake* mushroom and called it matsutake alcohol. Later this compound was identified as 1-octen-3-ol (Murahashi, 1938). Since then the compound 1-octen-3-ol has been identified in other feed and food sources including the essential oils of the families *Labiatae*, *Cupressaceae*, and *Agaricaceae* (Karrer, 1958). Honkanen and Moisio (1963) reported that this compound was the major volatile associated with clover flowers and leaves and at that time postulated that it could serve as a precursor of 1-octen-3-one which had earlier been identified as the compound responsible for a metallic off-flavor in dairy products by Stark and Forss (1962). In the case of dairy products, other researchers have reported a mushroom off-flavor resulting from lipid oxidation (Patton, 1962; Forss et al., 1960a,b; Stark and Forss, 1964). Hoffman (1962) also reported that 1-octen-3-ol was found in numerous oxidized lipid sources. 1-Octen-3-ol has also been identified in black currants (Andersson and von Sydow, 1964), cranberries (Anjou and von Sydow, 1967), and potatoes (Nursten and Sheen, 1974).

Researchers have reported that 1-octen-3-ol is the main volatile associated with certain mushroom species. For example, it represented 78% of the volatile fraction isolated from *Agaricus bisporus* (Wasowicz, 1974) and was found at levels of 66% of the volatile fraction in *Cantharellus cibarius*, 72% in *Gyromitra esculenta*, 49% in *Boletus edulis*, 70% in *Lactarius trivialis*, 90% in *Lac-*

tarius torminosus, 72% in *Lactarius rufus*, and 33% in *A. bisporus* (Pyysalo, 1976). Dijkstra (1976) also specifically measured 1-octen-3-ol concentration in 14 mushroom species and found a range from a low of <0.02 $\mu\text{L/L}$ of extract of dried *B. edulis* to a high of 190 $\mu\text{L/L}$ in *Calvatia gigantea* (giant puffball). Waowicz and Kaminski (1974) found 82% 1-octen-3-ol in *B. edulis*.

In the case of the Shiitake mushroom, *Lentinus edodes* lenthionin, a cyclic sulfur-containing compound having the formula $\text{C}_2\text{H}_4\text{S}_5$, has been identified as the primary odorant (Morita and Kobayashi, 1966; Wada et al., 1967). Yasumoto et al. (1976) reported that lenthionin can be enzymatically produced from lentinic acid.

In working with dried *B. edulis* Thomas (1973) reported on the identification of a series of pyrazine compounds. Because of their unique and potent aroma properties, (Maga and Sizer, 1973), they may be influential to the characteristic flavor of this product. To date, pyrazines have not been reported in other mushroom species.

Another interesting class of volatiles associated with a specific mushroom, *G. esculenta* or false morel, is a series of *N*-methyl-*N*-formylhydrazones which have proven to be highly toxic (Pyysalo, 1976; Pyysalo and Niskanen, 1977).

VOLATILE COMPOSITION AS INFLUENCED BY PROCESSING

Because fresh mushrooms contain numerous reactive classes of compounds, any form of processing usually results in significant changes in their overall composition including their volatile composition. Since fresh mushrooms are high in moisture, drying or dehydration has been the time honored way of preserving mushrooms. Sulkowska and Kaminski (1977) evaluated the effects of various drying methods using *A. bisporus*. Specific drying methods included air, freeze drying, fluidization, roller and spray drying. They reported that all drying methods resulted in losses of ~90% of 1-octen-3-ol. Dijkstra (1976) also reported major losses of 1-octen-3-ol in dried *A. bisporus* and the presence of only negligible amounts in dried *B. edulis* as compared to fresh as well as the total loss of 1-octen-3-one and *trans*-2-octen-1-ol in the dried product. In contrast, Thomas (1973) reported the presence of lactones, pyrroles, and pyrazines in the dried product that were not detected in fresh *B. edulis*.

Cooking can also result in major volatile changes. For example, Card and Avisse (1977) evaluated raw and cooked *A. bisporus* and found a higher proportion of carbonyl compounds in the cooked product. Picardi and Issenberg (1973) also used the *A. bisporus* species and compared the volatiles present in the raw product with the volatiles produced after cooking for up to 3 h. The major difference with heating was the appearance of 1-octen-3-one. By the technique employed in this study, this compound was not detected in the raw product but appeared after boiling for 15 min and reached its maximum concentration after 30 min of boiling. Thus, they suggested that the basic difference in flavor between raw and cooked mushrooms may be the level of 1-octen-3-one present.

As mentioned earlier, *N*-methyl-*N*-formylhydrazones (MFH), which are toxic, are associated with the fresh false morel (*G. esculenta*), and thus this species should be consumed in the dried or boiled state. However, as demonstrated by Pyysalo and Niskanen (1977), dried and boiled products can still contain measurable levels of these volatile compounds. For example, they reported that air drying of this species for 5 days reduced the MFH level to 12% of its original amount while drying for 10 days only reduced it to 10% of the original and drying for 14 days

Table I. Odor Descriptions of the Primary Volatiles Isolated from Mushrooms

compd	description	ref
1-octanol	sweet, detergent, soap	Pyysalo and Suihko (1976)
3-octanol	weakly nutty fungal like cod liver oil	Cronin and Ward (1971) Wasowicz (1974) Pyysalo and Suihko (1976)
3-octanone	sweet esterlike floral	Cronin and Ward (1971) Wasowicz (1974)
1-octen-3-ol	sweet, fruity, musty raw mushroom, butterlike fungal, resinous general mushroom mushroomlike	Pyysalo and Suihko (1976) Cronin and Ward (1971) Wasowicz (1974) Pyysalo (1976) Pyysalo and Suihko (1976)
<i>trans</i> -2-octen-1-ol	medicinal, oily	Pyysalo and Suihko (1976)
<i>cis</i> -2-octen-1-ol	oily, musty	Wasowicz (1974)
<i>trans</i> -2-octenal	sweet, phenolic	Pyysalo and Suihko (1976)
1-octen-3-one	fresh mushroom, metallic, fungal wild mushroom like boiled mushrooms	Cronin and Ward (1971) Pyysalo (1976) Pyysalo and Suihko (1976)
1-octen-3-yl acetate	mushroomlike, soapy water	Pyysalo and Suihko (1976)
1-octen-3-yl propionate	sweet, fruity, herbaceous, medicinal, mushroomlike	Pyysalo and Suihko (1976)

lowered it to 1.1%. Even after 180 days of room-temperature air drying, detectable levels of these compounds were still present. They also presented data showing that even product that was boiled for 10 min still had measurable levels and that the larger the amount of water used for boiling and the lower the pH, the greater the MFH loss. Thus, they cautioned that extreme care should be taken in the commercial and home processing of this particular mushroom.

FLAVOR PROPERTIES OF MUSHROOM VOLATILES

For the sulfur-containing compound, lenthionin, Wada et al. (1967) reported its odor threshold in water to be 0.27–0.53 ppm while in vegetable oil its threshold was 12.5–25 ppm.

Ney and Freytag (1978) evaluated the odor properties of a series of alcohols with the general formula R—CH(OH)CH=CH₂, with R varying from methyl to pentyl. They only found 1-octen-3-ol and 1-hepten-3-ol to have a characteristic mushroom aroma. In addition, a weak mushroom smell was noted for the saturated compound 3-octanol, but no such smell resulted from 1-octanol, 2-octanol, or 1-heptanol, thus indicating that mushroom aroma was highly dependent on the double bond and the 3 position of the hydroxy group.

Several groups have utilized sensory panels to evaluate mushroom species flavor differences. For example, Abbott and San Antonio (1974) compared *A. bisporus* and *Agaricus bitorquis* and reported that *A. bitorquis* had a stronger mushroom flavor. This can nicely be correlated to the higher 1-octen-3-ol level in *A. bitorquis* as compared to that in *A. bisporus* (Dijkstra, 1976). A sensory panel was also able to differentiate between dried Shiitake mushrooms that had been harvested at different times of the year (Matsumoto et al., 1979).

Cronin and Ward (1971) demonstrated that as with most flavor compounds, concentration significantly can influence the resulting odor sensation. At 10 ppm in water 1-octen-3-ol smelled like raw mushroom with a weak metallic note whereas at 1 ppm it was only a weak mushroomlike odor. They reported its odor threshold to be 0.1 ppm. In the case of 1-octen-3-one, a 10-ppm concentration resulted in a sweet sickly fungal smell with a strong metallic note whereas at 1 ppm a fresh mushroom with a weak metallic note resulted, while at 0.1 ppm a fresh uncooked mushroom note was apparent. They reported the odor threshold of this compound to be ~0.01 ppm. In addition, as is commonly done, they described the odor sensations emitted from the splitter of the gas chromatograph, and

various mushroomlike notes were detected in areas of the chromatogram where no peaks were visibly detectable, thus perhaps indicating that there are other as still unidentified compounds responsible for mushroom odor. Likewise, Picardi and Issenberg (1973) isolated various gas chromatographic fractions that had varying degrees of mushroomlike odor.

On the basis of flavor threshold data and actual concentrations of volatiles found in *Coprinus comatus*, Dijkstra and Wiken (1976b) concluded that 1-octanol (found 0.46 μL/L; threshold 0.1 μL/L), 3-octanol (found 0.5; threshold 0.1), 3-octanone (found 1.05; threshold 1), and 1-octen-3-ol (found 1.20; threshold 0.4) were present at sufficient levels to significantly contribute to mushroom aroma. The influence of optical activity of 1-octen-3-ol relative to mushroom flavor intensity has been evaluated (Dijkstra and Wiken, 1976a). They reported that the (–) form had a lower threshold in water (0.43 μL/L) than the (+) form (0.61 μL/L). In another report of theirs (Dijkstra and Wiken, 1976b), it was stated that naturally occurring 1-octen-3-ol is in the (–) form. Dijkstra and Wiken (1976a) have also reported that the threshold for 1-octen-3-one is 0.03 μL/L in water which is significantly lower than that for the corresponding alcohol, namely, 1-octen-3-ol.

Undoubtedly the most extensive investigation into the role of specific volatiles associated with mushrooms relative to their sensory properties was conducted by Pyysalo and Suihko (1976). Their odor descriptions of mushroom associated volatiles, as well as those of other researchers, are summarized in Table I. Odor threshold data presented by Pyysalo and Suihko (1976) for the 10 main volatiles that they isolated and identified from 7 fresh mushroom species indicated that 1-octen-3-one was one of the most potent compounds with a threshold of 0.004 ppm. A compound found to have even a lower threshold was *trans*-2-octenal (0.003 ppm), but it did not possess a typical mushroom odor sensation. In addition, 1-octen-3-ol (0.010 ppm), 1-octen-3-yl acetate (0.09 ppm), and 1-octen-3-yl propionate (0.022 ppm) had low thresholds that produced mushroomlike sensations. From their investigation Pyysalo and Suihko (1976) concluded that 1-octen-3-ol and 1-octen-3-one were the most important volatiles associated with the fresh mushroom species investigated. It was also noted that 1-octen-3-ol can serve as the precursor of 1-octen-3-one through oxidation.

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ARTICLES

Analysis of Simple Sugars and Sorbitol in Fruit by High-Performance Liquid Chromatography

Michael L. Richmond, Sebastiao C. C. Brandao, J. Ian Gray, Pericles Markakis, and Charles M. Stine*

The application of a high-performance liquid chromatographic (LC) procedure for the determination of sugars and sorbitol in fresh fruits is described. This system combines the use of two bonded phase carbohydrate columns, joined in tandem; a ternary mobile phase (acetonitrile-water-ethanol) and a differential refractometer to accurately and precisely separate fructose, glucose, sorbitol, sucrose, and maltose. Total analysis time was 20 min for the five-sugar mixture. Twenty-four fruits were analyzed including eleven from the family Rosaceae, which often contain sorbitol. Sample recoveries ranged from 98% for fructose to 102% for maltose.

Recently, Lee (1978) reviewed the many methods available for determining carbohydrates in foods. Carbohydrate analysis may be separated into the following categories: physical, chemical, colorimetric, and enzymatic. Of the different techniques available, enzymatic and

chromatographic (a physical method) procedures are most commonly used. The various chromatographic procedures include paper, thin-layer (TLC), gas-liquid (GLC), ion-exchange (IE), and more recently high-performance liquid chromatography (LC). Automated enzyme assays are also being used to determine carbohydrate content.

Huntington (1978) described the use of an enzymatic analyzer for determining glucose, sucrose, and lactose. Immobilized enzymes are used for the sugar assays and

*Department of Food Science and Human Nutrition, Michigan State University, East Lansing, Michigan 48824.