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Why do food and drink smell like earth?

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Fungi have long been associated with earthy odours. One of the main contributors to this odour is geosmin, a sesquiterpenoid metabolite produced by soil living fungi. Some food commodities are liable to contamination by geosmin producing fungi. Under favourable environmental conditions the production of geosmin occurs. One of the producers of geosmin in fruits is *Penicillium expansum* which also produces the mycotoxin patulin. Recent reports indicate that geosmin production by *P. expansum* is stimulated by *Botrytis cinerea*. However, the effect on patulin production is not known. The above issues will be discussed in this contribution.

Keywords geosmin; patulin; *Penicillium expansum*; *Botrytis cinerea*

1. Introduction

Some food and drink can smell earthy which is associated with the foods being “off”. However, other foods naturally have this odour, e.g. beet. Wines can have an off-smelling earthy nose. Although a low level of the note can be considered as attractive. Drinking water may have the taste and smell. Some fish have a noticeable earthy taint upon occasion and cured meat may have a similar odour. Edible mushrooms possess an earthy odour similar to cheeses such as camembert and stilton. What do most of these commodities have in common? Fungi.

Fungi form a fifth kingdom to the others approximately described as plants, animal, bacteria and algae/protozoa. They can be single cell (yeasts) or multicellular (filamentous fungi). Nutrition is absorbed through the well wall of the organisms allowing growth and multiplication. Incredibly, only 80000 species have been described from an estimated total of 1.5 million [1].

Fungi are of great benefit to mankind as they produce antibiotics, flavourings, industrial enzymes, and organic acids. Mushrooms, single cell protein and the synthetic protein, Quorn, are recognised foods or feeds. Fungi are used in cheese production (e.g., camembert), cured meats, alcoholic beverages, and bread making. The crucial environmental role is in recycling of organic plant material. Fungi "biodeteriorate" many commodities and sometimes create "off" odours: Mycotoxins may be produced in food and drink (e.g., wine). They are a cause of human diseases particularly those related to immunocompromised patients. Fungi have a devastating role as plant pathogens.

The taxonomy of fungi is confused. This is partly from the complicated life strategies and a lack of attention by researchers [2]: It has only recently that separate kingdom status has been achieved. An overemphasis on minor morphological features has created too many species which has resulted in numerous taxonomic revisions. *Penicillium* has had a particularly turbulent history in these regards.

A novel scheme for identifying penicillia has been developed by [3, 4] and breaks the mould of fungal identifications. Fungi are identified to a level that is well within operational limits (e.g., the branching system for terverticillate strains). In addition, the fungi are analysed for the relevant metabolite: The mycotoxin patulin was employed initially [4].

Fungi produce a range of secondary metabolites which are unrelated directly with the growth and reproduction of the organism. Broadly speaking secondary metabolites can be divided into volatile and non volatile representatives. Some of these compounds are specific to particular taxa whereas others are more universal. The chemicals have been used as taxonomic characters for a few fungi [5], although the

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volatile compounds are more experimental. In addition, the difficulty in identifying particular fungus, has encouraged the use of PCR methodology [6], although it suffers from a lack of suitable controls [7]. The title of this review poses another question.

What is the smell of earth? Odour is a sensation caused by odorant molecules dissolved in air: organic compounds provide the widest range of odours. This is followed by the psychological aspects as stimuli are processed in the brain. An objective and analytical measure of odour is impossible. Individual reactions are related to gender, age, state of health and personal associations. For most people, the process of smelling gives little information concerning the ingredients of a substance. Consequently, such notions as earthy odours are subjective, although tasting panels may help to make the process more objective.

Some food and drinks are claimed to have an earthy aroma. For example, beets and mushrooms are associated with the smell. However, the aroma can be described as mouldy and/or musty [8]. Isolates of *Penicillium discolor* were compared with other terverticillate penicillia using profiles of volatiles and were found to be distinct. *P. discolor* and *P. crustosum* were the only terverticillate *Penicillium* species that are able to produce geosmin and 2-methyl-isoborneol (MIB). Both of these volatiles were "known" to have musty/mouldy odours according to these authors, although they are also referred to as earthy smelling compounds (see below).

P. expansum and other species have long been associated with distinctive odours. *P. expansum* and *P. crustosum* have been described as "strong mouldy or earthy", *P. claviforme* and *P. olivino-vinde* as mouldy; *P. purpurogenum* as "fragrant apple" or “"walnut" smelling in old age”; *P. digitatum* like "spoiling citrus fruit" or "unpickled dill" and *P. decumbens* as "perfume like" [9]. The description of the smell of a fungus as "mouldy" is tautological and unhelpful as the term fungus and mould are often used interchangeably (you might as well refer to the smell of fungi as being fungal).

Furthermore, the odour of the metabolites associated with the smell has been variously referred to as earthy, mouldy, and musty. The smell of earth is evocative of fungi. Some of the smells from compounds produced by fungi are earthy, mushroomy, etc. Geosmin has an earthy smell and is produced by *P. expansum.* MIB is also earthy (or earthy-camphor) and is produced by *Botrytis cinerea* [10]. An earthy (or musty) nose can be determined from cheeses which have been inoculated with fungi (e.g., camembert, stilton, etc.) [11].

The earthy smell can be detected from foods and drinks contaminated with fungi, e.g. grapes. At low levels the smell is attractive although at high levels it is obnoxious. For example, the tasting notes to a Montlouis, Cuvée des Loups wine from a wine merchant's web site talks about "…touches of quince and earthy botrytis suggestions of dried apricot." Obviously, these are considered as good characteristics. Mycologists certainly do not need to be reminded that fungi are associated with the smell when growing cultures for investigation. Indeed the aroma has been employed as a character to identify certain species, although this practice needs to stop due to health and safety issues.

2. Geosmin

(-)-Geosmin (trans-1,10-dimethyl-trans-9-decalol) is an aromatic volatile metabolite with an earthy smell and is detected in grape products made with rotten grapes [12]. Humans are extremely sensitive to the smell of geosmin. Other similarly-smelling odoriferous compounds are also detected (see later). The enantiomer form, (+)-geosmin has less of an aroma and can be differentiated by chromatographic methods from (-) geosmin [13]. Geosmin is a common volatile secondary metabolite from fungi. However, the compound is also produced by bacteria and in particular the Actinomycetes. Certain algae produce geosmin. As mentioned, geosmin is present in beet vegetables [14], and a symbiotic earthy-smelling microorganism may be involved in producing the smell. Other surprising producers include fish which have become off. Furthermore, geosmin can impart an earthy taste and odour to water resources. The volatile continues to be detected from "new" fungal species [15]. The presence in grapes may require two fungi, *B. cinerea* and *P. expansum* [12]. Grapes may have a residual capacity to produce an earthy aroma *per se*.

There is remarkably little information concerning the toxicity of geosmin [16]. Nevertheless, there indications that it may act a repellent for certain insects such as millipedes [17]. It is not clear if it is the (+) or (-) form of geosmin is being analysed. For example it is not apparent that in [12] whether the geosmin detected in the grape or grape derived samples is one and/or the other.

3. *Botrytis cinerea* and *Penicillium expansum*

The ascomycete *Botrytis cinerea* [teleomorph *Botryotinia fuckeliana*] grows as a grey mould on a variety of commercial crops causing serious economic losses. It is known that the virulence of the fungus is severely affected by disruption of chitinase genes which are hence the sites of targets for novel fungicides [18]. In wine manufacturing it is referred to as grey rot. Interestingly, growth is encouraged in grapes to give the "noble rot". A recent paper associated the production of geosmin in grapes for wine from an interaction between the fungus *Penicillium expansum* [12] which is also a notorious rot of fruit and vegetables. *B. cinerea* was present in earthy-smelling grapes and the well-known geosmin producer *P. expansum* was "omnipresent".

4. Grapes

The earthy smell is of crucial importance to grapes and products. *B. cinerea* and *P. expansum* produce volatile compounds which affect grape and wine quality. For example, both produce earthy components. MIB and (-)-geosmin are two compounds responsible for the smell. Some of the smells have been referred to as mushroom, camphoric, mossy, mouldy or earthy. These aromas can also be detected by gas chromatography-olfactometry. Other compounds involved include 1-octen-3-one, 1-octen-3-ol, 2-octen-1-ol, and 2-heptanol and have associated smells and fungi responsible for the odours (Table 1) [10]. La Guerche *et al.* [12] interpreted the origin of geosmin from *P. expansum* in grapes which were also contaminated by *B. cinerea*. Furthermore, it was noted by the authors that there were at least two groups within *P. expansum* including from analysis of the internal transcribed spacer (ITS) DNA region [10, 19]. In addition, many species listed was attributable to more than one smell (including no smell) and that the smell was consistently linked to the detection of compounds by gas chromatography (GC). *P. expansum* alone was able to produce geosmin on a model medium but not on grape juice medium (GJM). However, geosmin production by *P. expansum* was demonstrated on GJM after pre-culture of *B. cinerea* [12]. So why does this occur?

Presumably, *B. cinerea* preconditions the medium for geosmin production. Geosmin production may be a defence response to *B. cinerea* to enable *P. expansum* to compete with the other fungus. *P. expansum* may then be able to colonise the substrate and produce mycotoxins (e.g., patulin) to "secure" the substrate. The interactions are likely to be complex involving the (a) host plant, and (b) competing fungi, bacteria and insects. The contribution of the host is demonstrated by the *Arabidopsis*/*Botrytis* interactions which are complex involving the formation of secondary metabolites by the plant [20]. A similar situation may occur in vines and grapes.

A more satisfying scenario is that inhibition of geosmin synthesis occurs in *P. expansum*. The phenolic components of grapes [10] may inhibit *P. expansum* (and hence patulin production) by inhibiting geosmin production and permitting precursors toxic to *P. expansum* to accumulate. Growth of *B. cinerea* in the grapes is possible because laccase [16] converts the phenolic compounds to quinones. The phenolics, hydroxycinnamic acids, anthocyanins and flavanols are oxidized by polyphenol oxidase activity of *B. cinerea*. The resulting quinones are highly reactive with grape glutathion. Thus geosmin inhibition may be relieved by the action of *B. cinerea* permitting *P. expansum* to grow and for the production geosmin to become established. *P. expansum* may then produce metabolites such as patulin to secure the substrate from other microbes which will be in contact with the compound as it is secreted into the substrate. The pheromone-like volatility of geosmin could prevent insect competition for the substrate: Geosmin caused a negative tropic response in millipedes for example [17]. This is but one possibility which may merit further investigation.

Table 1 Fungi isolated form rotten grapes with various aromas or none [10].

Fungus	Nº of strains	Odour	Associated volatile
Aspergillus Section *nigri*	1	mushroom	1-octen-3-ol 1-octen-3-one
B. cinerea	7	none	
	32	earthy camphor	MIB
	35	mushroom	1-octen-3-ol 1-octen-3-one
	1	mushroom	Unknown
Coniothyrium sp.	1	mushroom	Unknown
	1	earthy camphor	MIB
P. brevicompactum	1	mushroom	1-octen-3-ol 1-octen-3-one
P. carneum	1	earthy	Geosmin
P. citreonigrum	1	cellar	Unknown
P. decumbens	1	earthy	Geosmin
P. expansum	49	earthy	Geosmin
P. miczynskii	2	earthy	Geosmin
P. pinophilum	1	earthy	Geosmin
P. purpurogenum	3	camphor	Unknown, "KI 1479"
	1	earthy	Geosmin
	1	cellar	Unknown
P. thomii	8	none	
	3	mushroom	1-octen-3-ol
	3	earthy camphor	MIB
R. nigricans	1	earthy camphor	MIB

Phytotoxins have been isolated from *B. cinerea* indicating strongly how the fungus causes the disease [21]. The sesquiterpenoid botrydial is the most known and active, and causes the typical lesions of the fungal infection: The metabolite plays an important role in the pathogenicity of the organism in vivo. Fruits of *Capsicum annuum* were demonstrated to contained botrydial, as were the leaves of *Phaseolus vulgaris* and *Arabidopsis thaliana* inoculated with the fungus. In addition, botrydial regulates the growth of the fungus as growth ceases at high levels of the compound. Growth re-commences after the biodegradation of botrydial by the fungus to less potent phytotoxins. These observations have high implications for infection of plants and persistence of the compounds in the food chain.

5. Grapes - Other compounds

MIB is a metabolite of *B. cinerea*, penicillia and *Streptomyces* and has a similar smell to geosmin (see Table 1). MIB was detected in rotten Merlot grapes. The compound was only found in black grapes, unlike other odour compounds such as fenchone and fenchol. MIB was also detected in musts made with black grape varieties, but not in botrytized Sémillon musts. Moreover, MIB has not been reported in wine. Finally, the compound was detected in wine with cork taint; an important observation for cork producers such as Portugal.

6. Patulin

Patulin is the classic compound which was employed to established many concepts within fungal secondary metabolism. Patulin is associated with *P. expansum*. The compound is known to contaminate apple products and the fungus is responsible for the blue rot of apples. *P. expansum* is also responsible for a rot of grapes and patulin can be found in grape products. It is interesting to explore links between geosmin and patulin production in grapes.

Patulin is a mycotoxin [22]. Mycotoxins are fungal metabolites which are found in food and drink naturally from the growth of filamentous fungi. The presence of patulin is associated with fruit and vegetables and was investigated an antibiotic against fungi. However, the compound is too toxic for it to be a useful pharmaceutical. It is known to inhibit *Saccharomyces cerevisae* when used to produce alcohol commercially, and is broken down by the yeast during fermentation. Patulin is a small lactone molecule produced *via* the polyketide metabolic pathway of various fungi including members of *Penicillium*, *Aspergillus*, *Paecilomyces* and *Byssochlamys*. Interestingly, there a citation of patulin being produced by a *Botrytis* species, i.e. *B. allii* [23] and other species need to be tested for this ability, including *B. cinerea*. Other (unconfirmed) citations are available for *Botrytis* (e.g., Food information site Wageningen University http://www.food-info.net/uk/index.htm). In addition, *P. expansum* produces other mycotoxins and *B. cinerea* also produces secondary metabolites which are thought to inhibit fermentations by *S. cerevisae* in wine production. Finally, patulin has been described as possessing an earthy odour but this was surely a mistake (see [6]).

7. Metabolic pathways of geosmin and patulin

Geosmin (Figure 1) is a sesquiterpene derivative. Existing evidence indicates that geosmin synthesis involves a sesquiterpene precursor, possibly mixed function oxidase activity and L-methionine. Although the intermediates involved in geosmin synthesis have not been reported, the pyrophosphate ester of farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol) is considered the universal precursor of sesquiterpene-derived metabolites.

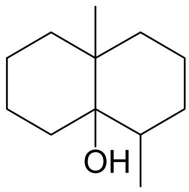

Fig. 1 Chemical structure of geosmin.

On the other hand patulin (Figure 2) is a small lactone molecule derived form the polyketide pathway via acetate. The metabolic pathway has been well determined. The two pathways for geosmin and patulin are different and substrates for each pathway are not in competition with each other. The total carbon pool would require being available for either route. Neither compound involves nitrogen and so there is no intrinsic demand for the nitrogen pool for these compounds.

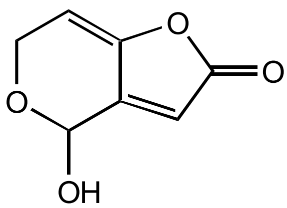

Fig. 2 Chemical structure of patulin.

8. Factors affecting production

The conditions that stimulate patulin production are not necessarily the same as those for growth of the fungus. One consequence of this is that a high amount of biomass of *P. expansum* may not imply that there is a high concentration of patulin. It is reasonable to assume that a low amount of biomass will imply a low amount of patulin. Related to this, [10] demonstrated that *P. expansum* was isolated frequently from rotted grapes that had an off odour. So the implication is that the odour is present because there is a large amount of *P. expansum* biomass. Hence patulin may also be present. Equally, *B. cinerea* is known to produce a wide-range of metabolites, some with known biological activity (see above) and involved intimately with pathogenicity.

Paterson [24] indicated that patulin could be stimulated by the use of glucose analogues such as 2-deoxy-D-glucose and fungicides. Production of patulin is highly influenced by nutrient quality and quantity. There is no direct evidence for patulin inhibiting *B. cinerea*. Furthermore, to reduce algal populations and associated biosynthesis of geosmin, copper sulphate is often applied to aquatic systems. Cultures of *P. expansum* grown on increasing concentrations of copper sulphate accumulated more biomass than untreated controls. In addition, copper-treated mycelium contained greater concentrations of geosmin than untreated controls [25]. Such phenomena need to be borne in mind when applying fungicides to fruit etc. Interestingly, the bacterium *Burkholderia cepacia* produces a compound which inhibits *B. cinerea* and may be a possible control compound [26]. This demonstrates that *B. cinerea* can be controlled by a compound other than commercial fungicides and which is produced biologically.

Geosmin and patulin are known to be sensitive to physical/chemical conditions. The addition of sulphur dioxide generating compound, at normal levels (100 mg/L) to a sample containing 25 mg/L of patulin caused the patulin to decrease to about one-half in 15 min [27]. Geosmin degrades to aroma-free metabolite in acidic conditions. Patulin is also sensitive to pH and other conditions such as proteins with cysteine residues, and sulphur dioxide in general. Patulin is normally considered to be degraded to other compounds during fermentation and so may not be expected to be present in wine. The effect of fungicides needs to be considered on mycotoxin and geosmin production as do other control methods such as biocontrol.

Patulin production in culture has been shown to occur when growth rate diminishes because of limitations on cell growth such as nitrogen consumption [28]: there is no equivalent information for geosmin. It is clear that patulin is increasingly stable at low pH [29], geosmin tends to degrade to a compound without an odour, and so if was produced in such circumstances it would not accumulate.

Many biocontrol fungi have been used as potential controls for the *B. cinerea*. *Trichoderma hiazaria* is perhaps the most cited at the present time. Various others have been suggested including representatives of the penicillia. A preparation of *T. harzianum* was sprayed on cucumber plants in greenhouses in order to control fruit and stem grey mould. Biological control of grey mould was also suggested by Newhook [30] who sprayed tomato plants with *Cladosporium herbarium* and *Penicillium* sp., reducing the incidence of grey mould of fruits. Sufficient control of *B. cinerea* by isolates of *Trichoderma* and *Gliocladium* spp. was reported on grapes [31]. Biocontrol of *P. expansum* is also suggested [24].

Increasing concentrations of $CaCl_2$ (25-175 m*M*) resulted in decreased spore germination and germ-tube growth of *B. cinerea* and *P. expansum*. The greater effect was observed with *B. cinerea*. Glucose overcame the inhibitory effect. $MgCl_2$ (25-175 m*M*) had no effect on these parameters, indicating that the calcium cation rather than the chloride anion was responsible. The pectinolytic activity of crude enzyme obtained from the culture medium of both pathogens was also inhibited by CaC_2, and with the greatest effect on the crude enzyme from *P. expansum*. Obviously, the pectinase effect may be independent of the spore and germ-tube effect from this observation. Further, the biocontrol activity of *Candida oleophila* was enhanced by the addition of 90 or 180 m*M* $CaCl_2$. The effect of *C. oleophila* in the presence of calcium ions was due to the inhibitory effects of the ions on pathogen spore germination and metabolism. It was also demonstrated that, when using the antagonist *Pseudomonas syringae*, the addition of specific amino acids (L-asparagine and L-proline) enhanced biocontrol activity against *P. expansum*. This was from the ability of the bacterium to out-compete the fungus for the nitrogen source, leading to enhanced growth of the bacterium in wound sites. Several other amino acids that were selectively utilized by the antagonist and not by the pathogen [32]. It would of course be useful to test *B. cinerea* under such conditions to compare with *P. expansum*. In general, the effects on patulin and geosmin production need to be determined.

The effect on (-)-geosmin and MIB during alcoholic fermentation of must and storage in model solution was investigated (although there did not appear to be uninoculated controls for the experiment). Only 20% of the geosmin in a botrytized Sémillon must disappeared after 2 weeks of alcoholic fermentation. (-)-Geosmin was stable during alcoholic fermentation and storage, especially at the optimum temperature for aging wine (15 ºC). However, 90% of geosmin disappeared in a model solution after 24 h at 90 ºC. Geosmin degradation is apparently highly dependent on temperature. Geosmin chemical transformation leads to argosmin, a much less odorous compound. In a model solution, the MIB concentration decreased by 80 and 100% after only 7 and 20 days respectively at 20 ºC [10]. It would be interesting to compare these data with patulin in wine.

Towards this end, patulin was very stable in grape juice or grape wine with no significant change for 1 month at room temperature, or 2 months in the frozen state. Furthermore, it disappeared rapidly during fermentation to zero [27].

9. Analysis

In general, and in much of the literature, there is a tendency to confuse non detection of geosmin with non production (see [3]). When the compound is not detected it obviously does not mean it is not produced.

9.1 Chromatography

The analyses of patulin and geosmin are conventional if different. Patulin can be detected by liquid chromatography (LC) and predictable geosmin by GC based methodology. Thin-layer chromatography, (TLC), LC and high performance liquid chromatography (HPLC) have all been employed for patulin. Diode array detection is particularly useful to provide further differentiating characters for the compound. Due to the volatility of geosmin, GC based methods are employed which are fairly conventional. Coupling with mass spectrometry is increasingly used for the compound. In addition, GC with aroma testing is employed, which is an interesting combination of human senses with a machine. As geosmin occurs in the two forms ((-) and (+)), there are also GC based methods that can separate these to compounds.

A fluorometric scanning technique for grapes and products was developed to measure patulin samples separated by two dimensional TLC. The chromatographed samples were extracted and purified prior to separation [27]. Patulin in apple and grape juice was extracted with an Extrelut column and a quantitative determination was made by HPLC or TLC with lower limits of 5 and 20 ppb respectively [33]. Grape juices and wines produced were analyzed for patulin and patulin was present in the juices but not was detected in a partially fermented juice and the wines [34]. As mentioned, an intriguing method for analyzing aromas is GC olfactometry. Essentially this is GC coupled with a human "sniffer" [10]. It can suffer from problems such as a small amount of odour compound being masked by a non-odour compound, or odour clusters where odours can be coeluted. Also, the human factor needs to be considered both in terms of (a) subjectivity and (b) health and safety.

9.2 PCR

The use of PCR (polymerase chain reaction) to detect fungi has developed rapidly. However, they have not been applied appropriately in many cases with fungi [7]. An interesting development in detecting the potential for patulin production is to use the metabolic pathway employed to obtain the final compound. In the case of patulin the *idh* gene has been most developed [6]. The probe has been employed in a culture independent probe in orchards with obvious implications for vineyards. Further developments have occurred in terms of sequencing the gene from various species with the intention of obtaining specific probes for species. Equivalent primers are not available for geosmin. Various PCR methods have been developed for the actual fungi. Methods for *P. expansum* are described in [6, 7], and similarly for *B. cinerea* [35, 36].

9.3 Health and safety

An issue which needs to be addressed in this type of work is of a health and safety nature. Because of the know toxicity of fungal secondary metabolites cultures should be smelled for their aroma which is indefensible in terms of health and safety. By analogy, the smelling of grape-juices and wines for these same compounds is surely questionable, and requires assessment [15].

10. Conclusions

The production of earthy odours in food is a complex subject. In wine the presence of the smell can be considered either detrimental or desirable. Similarly, the rot by *B. cinerea* can be the notorious grey rot of grapes or the much sought after noble rot. The earthy odour is complex also with not only geosmin being involved. *B. cinerea* produces earthy smelling compounds as does *P. expansum*. The rot by *P. expansum* is wholly undesirable as is the production of patulin in grapes and products. Also, it produces geosmin which remains in the fermentation of wines longer than MIB. There is evidence that *Botrytis* species can produce patulin and this needs to be assessed as this fungus could be the source in grapes and products, as could *P. expansum*. Thus, more research is required to determine which fungus is involved in patulin and earthy-smell production in grape products. There does not appear to be a link between the metabolic pathways of geosmin and patulin except that they both require sources of carbon but not nitrogen. Various physical/chemical/biological factors differentially affect geosmin and patulin and the respective producing organisms. Geosmin and patulin require GC and LC methods methodology respectively.

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