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ARSENIC ACCUMULATION IN SOME HIGHER FUNGI

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The high arsenic concentrations reported in literature for *Laccaria amethystina* were amply confirmed. In addition, it was demonstrated that *Laccaria fraterna* also accumulates the element, whereas in other species of *Laccaria* the phenomenon was far less outspoken. Few other basidiomycetes proved to have an affinity for the toxic element. The arsenic concentrations in the principal edible mushrooms of commerce were found to be very low, i.e. on the average 0.5 mg/kg on dry matter. Among the ascomycetes *Sarcosphaera coronaria* was recognized as an accumulating species. The arsenic content of four collections ranged from 360–2130 mg/kg with an average of 872 mg/kg on dry matter.

Many species of higher fungi from various genera are capable of accumulating trace elements including several potentially toxic metals (for reviews, see Stijve, 1980 and Seeger, 1982). So far, very few fungi have been reported to concentrate arsenic from their substrate. Byrne, Ravnik & Kosta (1976) analysed a number of fungi from different genera for this toxic element and found an average concentration of 1.3 mg/kg on dry matter, which is rather low. However, they observed significantly higher levels in *Amanita muscaria* (L.: Fr.) Hook., *Lycoperdon perlatum* Pers.: Pers. and especially in *Laccaria amethystina* Cooke.

This edible common species, sold on the markets in Switzerland, but of minor culinary importance, was found to contain up to 200 mg/kg on dry weight, a really staggering figure (Byrne & Tusek-Znidaric, 1983) if one considers that most vegetable foods contain a 1000 times less. Meanwhile, several other fungi have also been analysed (Allen & Steinnes, 1978) but no additional arsenic accumulators have been reported. It should, however, be noted that, on the whole, the arsenic content of fungi has not been subject of a systematic search. To the authors' knowledge a mere 35 species have been analysed, i.e. far less than the 236 screened for mercury and the 402 for cadmium (Seeger, 1976 and 1978).

Moreover, virtually nothing is known about the trace element content of all those fungi of which the botanical determination is difficult. For example, there are almost no data for the genera *Cortinarius* Fr. and *Entoloma* (Fr.) Kumm., to say nothing about those fungi that are generally known as LBMs (Little brown mushrooms).

Although *Laccaria amethystina* was recognized as an accumulating species more than 13 years ago, the high levels reported have never been checked elsewhere, nor has the search been extended to other members of the genus *Laccaria* B. & Br. in spite of the fact that several of these fungi have a world-wide distribution. Consequently, the present authors undertook a study of the arsenic content of common and rare *Laccaria* species gathered mostly in

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European countries. In order to check whether arsenic accumulation is specific for *Laccaria*, a selection of other higher fungi among which several ascomycetes were included in the investigation.

Experimental

The fungi studied were mostly gathered between 1985 and 1988 at various sites in the Netherlands, the German Federal Republic, Switzerland and France, although for the most rare *Laccaria* species, material was also obtained from Australia. Since *L. amethystina* is an edible mushroom for sale at markets in Switzerland, we included a number of samples purchased at two weekly intervals.

Arsenic was determined by hydride generation atomic absorption spectrometry (AAS) as described in the Manual of the Association of Official Analytical Chemists (1984).

Reliability of the results was ascertained by subjecting selected samples to neutron activation analysis, which was carried out by the direct (non-destructive) method: 0.6–1 samples were sealed in vials and irradiated for 30 minutes in a 'swimming pool' type reactor (capacity 2 KW/h) producing a flux of 10^9 thermal neutrons/cm^2.s. Gamma spectrometric analyses were performed after 20 hours and again after 2 days by measuring the decay of ^{76}. As at 559 KeV using a high resolution Ge-detector.

Results and Discussion

Fungi in general and edible mushrooms

A limited survey encompassing 16 genera of basidiomycetes (Table I) largely confirmed the observations made earlier that arsenic levels in fungi are generally low (Byrne, Ravnik & Kosta, 1976; Allen & Steinness, 1978). Only one collection of *Sarcodon imbricatus* (L.: Fr.) P. Karst., an edible species, was found to contain 22.4 mg/kg, but its origin could not be ascertained, since it was bought on a market. This finding prompted us to examine the principal edible mushrooms of commerce for their arsenic content, but, here again, the results were quite unremarkable (Table II), although the average concentration is somewhat higher than that of most foods of vegetable origin which rarely exceeds 0.25 mg/kg (Ishinishi & al., 1986).

The genus Laccaria

A total of 37 samples representing seven species of *Laccaria* were analysed (Table III). The arsenic-accumulating ability of *L. amethystina* was amply confirmed, although the wide fluctuations in the concentrations are striking. There is little doubt that *L. fraterna* (Sacc.) Pegl. also concentrates important quantities of the toxic element, but the accumulating power of the other species is difficult to appreciate. It is not unthinkable that *L. laccata* var. *pallidifolia* (Peck) Peck and *L. purpureobadia* D. Reid possess the faculty to concentrate arsenic, but that they will only do so under certain as yet unknown conditions. Collections of both species that contained the highest levels were gathered at sites where the soil concentration was definitely lower, i.e. 1.5–2 mg/kg.

Ascomycetes

Upon analysing a number of ascomycetes, the arsenic content of *Morchella* Dill.: Pers., *Gyromitra* Fr., *Helvellaceae,* and a number of cup fungi was found again rather low with the notable exception of that of *Sarcosphaera coronaria* (Jacq.) Boud., which even exceeded the high concentrations reported in *L. amethystina* (Table IV).

Sarcosphaera coronaria is popularly known as the Crown fungus. Its initially hypogeous fruit-bodies split open at maturity to form crown-like cups. In Europe the fungus is encountered in calcareous areas mainly under conifers, although it has also been recorded to grow in beech forests (Brandrud & al., 1986).

Several popular handbooks list it as edible, but some report that it has occasionally been responsible for intoxications. So far, we have never seen it on German or Swiss markets.

Confirmatory analysis

The almost absurdly high arsenic levels encountered in some species prompted us to subject a number of samples to confirmatory analysis by the neutron activation technique. For this purpose, we selected a series covering a concentration range of 0.5–400 mg/kg on dry weight.

The data listed in Table V indicate excellent agreement between the results found by both methods, and confirm the extremely high levels in both *Laccaria amethystina* and *Sarcosphaera coronaria* beyond reasonable doubt.

Conclusions

The high arsenic concentrations in *L. amethystina* reported earlier by Byrne, Ravnik & Kosta (1976) were readily confirmed. In addition, it was demonstrated that a member of the same genus, *L. fraterna,* also accumulates the element. However, few basidiomycetes seem to share this ability. The arsenic content of the principal edible mushrooms of commerce proved to be remarkably low.

Another isolated accumulating species, *Sarcosphaera coronaria,* was found among the ascomycetes. Its arsenic content (determined in four collections of various origin) proved to be about 300 times higher than that of fungi in general. It remains yet to be investigated in how far other cup fungi, such as *Discina* (Fr.) Fr., *Disciotis* Boud., and *Geopora* Harkn., are able to concentrate the toxic element. It is interesting to note that 47 mg/kg arsenic was found in a single *Geopyxis* species, but this observation should be confirmed.

Nothing is yet known about the form(s) in which arsenic occurs in the said mushrooms. *Laccaria amethystina,* although of minor culinary importance, is often sold on the Swiss markets, and it could well be that the arsenic ingested with this mushroom is probably not very toxic. Byrne & Tusek-Znidaric (1983) found that the element was present in a readily extractable, possibly ionic form, associated with low molecular weight substances. It is not unthinkable that this and other arsenic-accumulating fungi contain arsenobetaine and/or arsenocholine, two compounds occurring in several marine organisms (Ishinishi & al., 1986). The authors hope to verify this hypothesis at the earliest opportunity.

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Table I. Arsenic in various higher fungi

Species	Number of samples	Range in mg/kg on dry matter
Clitocybe div. spec.	12	0.14–0.53
Clathrus cancellatus Tourn.: Fr.	1	0.45
Strobilomyces floccopus (Vahl: Fr.) P. Karst.	1	0.37
Clitopilus div. spec.	3	0.99–2.3
Hygrophorus div. spec.	8	< 0.03–2.74
Squamanita odorata (Cool) Imbach	1	0.60
Macrolepiota div. spec.	3	1.2–4.0
Amanita div. spec.	6	0.2–1.85
Lactarius div. spec.	8	0.1–1.52
Russula cyanoxantha (Schaeff.) Fr.	2	0.06–0.09
Cortinarius div. spec.	4	0.81–1.2
Coprinus div. spec.	3	0.15–0.75
Agaricus div. spec.	3	0.15–0.45
Leccinum scabrum (Bull.: Fr.) S.F. Gray	2	< 0.2
Hydnum (Sarcodon) div. spec.	4	0.35–22.4
Polyporus div. spec.	3	< 0.05–0.2

Table II. Arsenic in edible mushrooms of commerce (1982–1987)

Species	Number of samples	Range in mg/kg on dry matter (average in brackets)
Agaricus bispora (J. Lange) Pilát (cultivated white mushrooms)	24	0.05–1.50 (0.50)
Boletus edulis Bull.: Fr. (dehydrated)	11	0.25–1.16 (0.50)
Suillus luteus (L.: Fr.) S.F. Gray (dehydrated)	4	< 0.04–0.26
Cantharellus cibarius Fr.: Fr.	6	0.13–1.30 (0.51)
Morchella esculenta (L.) Pers.	5	0.07–0.89 (0.58)
Auricularia spec.	6	0.08–0.50 (0.22)

Table III. Arsenic levels in members of the genus *Laccaria*

Species	Number of samples	Range in mg/kg on dry matter (average in brackets)
L. laccata var. *pallidifolia*	10	0.43–81 (10.9)
L. bicolor (Maire) P.D. Orton	4	0.28–1.17 (0.71)
L. proxima (Boud.) Pat.	3	0.22–0.66 (0.39)
L. tortilis (Bolt.) Cooke	1	0.39
L. amethystina	11	16–250! (92)
L. fraterna	4	23–266! (129)
L. purpureobadia	4	1.2–6.8 (4.3)

Table IV. Arsenic in some ascomycetes

Species	Number of samples	Range in mg/kg on dry matter (average in brackets)
Morchella esculenta	7	0.07–0.92 (0.61)
Gyromitra esculenta (Pers.) Fr.	2	2.0–2.5
Peziza vesiculosa Bull.: Fr.	2	< 1–2.8
Peziza badia Pers.: Fr.	pooled sample	< 1
Aleuria aurantia (Pers.: Fr.) Fuck.	2	< 1–8.0
Geopyxis carbonaria (Pers.: Fr.) Sacc.	1	47!
Sarcosphaera coronaria	4	360–2130! (872)
Helvella lacunosa Afz.: Fr.	1	0.31
Helvella crispa (Scop.) Fr.	1	0.60
Hevella elastica Bull.: Fr.	1	0.28

Table V. Confirmatory analysis by means of the neutron activation technique

Species	Values found by AAS (in mg/kg on dry matter)	NAA
Helvella crispa	0.67	0.60
Laccaria laccata var. *pallidifolia*	4.3	4.2
Sarcodon imbricatus	23.4	22.6
Laccaria amethystina	186	213
Sarcosphaera coronaria (collected in Fribourg)	405	402
Sarcosphaera coronaria (collected in Puidoux)	372	360

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