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A Spectroscopic Study of Vanadium in Mushroom

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ABSTRACT

Nine different species of mushroom were analysed spectrometrically for their vanadium contents. It was found that some edible species of mushroom, such as Agrocybe *and* Leutinus, *contain vanadium in amounts either comparable with, or higher than, the amounts in some poisonous species. The result suggests that there is no correlation between the vanadium content of the mushroom species examined and their toxicity.*

INTRODUCTION

'Mushroom' and 'toadstool' are terms applied rather loosely to the fruit bodies of fleshy gill-fungi and are commonly used to denote edible and poisonous species, respectively. They form a small part of the enormous range of organisms called fungi. Their essential characteristic is the lack of the green pigment (Pergler, 1981) and this puts the fungi in a separate kingdom from plants.

Structurally, the mushroom is like an umbrella with a cap protecting the spore-producing surfaces (the gills) from the rain. Edible mushrooms have a high nutritive value—almost twice that of any other vegetable or fruit. They are also rich in vitamins B and D. The edible species of mushroom include Boletus, Miller, the Parasol mushroom and the Chanterelle. Apart from the food value of mushroom, its medicinal value as an ideal food for diabetics and in cancer therapy has been emphasised (Geuders, 1974).

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Some species of mushroom, e.g. *Amanita muscaria*, are known to concentrate vanadium (Beinert & Palmer, 1965; Kneifel & Bayer, 1973). Whilst vanadium has been shown to be an essential trace metal (Schwarz & Milne, 1971), the toxic effects of the metal in animals are well known (Underwood, 1971; Berg & Lawrence, 1971; Johnson *et al.*, 1974). Mushroom poisoning is clinically subdivided into eight categories (Pergler, 1981). We therefore decided to determine the level of vanadium in both edible and poisonous species of mushroom and to investigate the correlation, if any, between the vanadium level and toxicity of mushroom. This paper reports the results of our investigation.

MATERIALS AND METHODS

Instrument

A Pye Unicam SP6-550 digital UV–visible spectrophotometer and a PT1–15 digital pH meter were used for the measurement of absorbance and pH, respectively.

Preparation of solutions

All reagents and chemicals used in this study were of the AnalaR grade and were purchased from BDH Chemicals Ltd, Great Britain.

Standard vanadium solution
A 100 mg per millilitre stock solution of vanadium was prepared from ammonium metavanadate and a 10% (v/v) solution of concentrated sulphuric acid in distilled water. Weaker standard solutions were prepared by suitable dilution.

8-Quinolinol solution (0·5%)
0·50 g of 8-quinolinol was dissolved in 100 cm^3 of alcohol-free chloroform and stored in a dark glass bottle.

Procedure

Most colorimetric and spectrographic methods for the determination of vanadium (Bertrand, 1942; Daniel *et al.*, 1942; Vogel, 1970) were found

to be unsuitable as they were insensitive to samples of high ash content. A modified method of two other investigations (Talvite, 1953; Nadalin & Brozda, 1960) using a vanadium specific complexing agent, 8-quinolinol, was adopted in this investigation.

Ten cubic centimetres of six standard solutions of vanadium (as vanadate), with concentrations ranging from 1 ppm to 10 ppm, were each pipetted and made up to 60 cm^3 in a 100 cm^3 beaker. The pH of the solutions was adjusted to 5·5 (pH of maximum extraction) by the addition of 4M ammonia solution or 2M sulphuric acid, as required. The solution was then extracted twice with two 5·0 cm^3 portions of chloroformic solutions of 8-quinolinol after the addition of 1·0 cm^3 of calcium versenate solution. The absorbances of the combined chloroformic extracts were read at 550 nm. A calibration curve of absorbance values against vanadium concentrations gave a straight line passing through the origin. In order to ascertain the authentic nature of the 8-quinolinol complexes formed, a complete UV–visible spectral scan (200–800 nm) was carried out for each solution and comparisons were made with literature spectra.

A known weight of fresh mushroom ($\leq$40·0 g) was dried to constant weight at 100–110 °C and charred at 400 °C. Charred mushroom was ground to powder and ashed in a viotresil crucible at 600 °C in a Gallenkamp hot spot muffle furnace for 6–7 h. The weight of the ash was determined on cooling in a desiccator. About 0·4 g of the ash in a 100-ml beaker was dissolved in 10·0 cm^3 concentrated hydrochloric acid and evaporated to dryness in a fume cupboard. This was followed by the addition of 10·0 cm^3 of 10% sulphuric acid. The resulting solution was heated to boiling and drops of 0·1M potassium permanganate solution were added until a permanent pink colour appeared.

The hot solution was neutralised with 0·1% methyl orange, the nearly colourless solution was diluted to 60·0 cm^3 with distilled water and the pH was adjusted to 5·5 with 4M ammonia solution and 2M sulphuric acid. The resultant solution was extracted twice with 1·0 cm^3 calcium versenate solution and 5·0 cm^3 of 8-quinolinol in chloroform.

The absorbance of the extract was read at 550 nm using 0·5% 8-quinolinol solution as a reference. The concentration of vanadium, in ppm, in each sample solution, was read from the calibration curve. Hence, the concentration of vanadium per gram of ashed mushroom was calculated.

RESULTS AND DISCUSSION

The results obtained during this study are summarised in Table 1. The concentration per gram of the ashed mushroom is adopted in this work as a reliable quantity for comparison purposes. This is because, to obtain the ashed mushroom, it would have been charred and dried to constant weight before analysis and is, therefore, not amenable to the influences of external physical conditions such as temperature, humidity or vapour pressure of the atmosphere or to the texture of the mushroom, which is intimately related to the moisture content. It should be mentioned, however, that the time between the collection of mushroom species and their analysis may also affect the concentration.

The comparatively small amount of ash resulting from the ashing of a large amount of the fresh mushroom indicates the presence of a large amount of organic matter or moisture in the mushroom.

Another interesting aspect of the results is that different types of the same species differ considerably in their vanadium contents.

The vanadium contents of some of the mushroom species classified as being edible compare very well with those of the poisonous species. As can be seen from Table 1, some edible species contain slightly greater amounts

TABLE 1
Levels of Vanadium Residues in Some Mushrooms

Mushroom species	*Weight of fresh mushroom (g)*	*Weight of ashed mushroom (g)*	*Absorbance ±0·001*	*Amount of vanadium (milligrams per gram of ash)*
(i) Edible				
Leutinus	22·925 3	0·255 7	0·012	44·6
Agrocybe	1·563 4	0·266 9	0·020	67·4
Agaric (type 1)	4·484 5	0·135 4	0·028	177
Agaric (type 2)	6·806 4	0·360 5	0·031	81·5
Termitomyces ctypeatus	9·293 7	0·737 0	0·046	56·9
Agaricus hortensis	138·880 7	0·325 4	0·026	73·7
(ii) Poisonous				
Volvariella	16·852 6	0·693 3	0·030	35·5
Lepiata (type 1)	39·319 8	0·788 9	0·022	26·6
Lepiata (type 2)	10·020 8	0·325 2	0·028	73·8

of vanadium than are found in the poisonous species. No correlation therefore exists between the vanadium content of a species and toxicity.

It has been reported that the toxicity of some poisonous species is due to the presence of toxins. *Amanita phalloides* contains the toxin phallotoxin which is chemically made up of α-amanitin and β-amanitin (Genest *et al.*, 1968; Faulstich *et al.*, 1974) which are cyclopeptides (Wieland, 1968) and do not contain vanadium. Our results also suggest that vanadium is not responsible for the toxicity of poisonous mushrooms.

The interference of certain elements was investigated by testing the vanadium recoveries in their presence. Reasonable amounts of these metals—except tin, titanium and tungsten—do not interfere. Because these metals, if present, in ash, were always only so in trace amounts, it was concluded that the 8-quinolinol method could safely be applied.

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