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SHORT REPORTS

ELECTRON SPIN RESONANCE OF VANADIUM IN *AMANITA MUSCARIA*

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Key Word Index—*Amanita muscaria*, Agaricaceae, fly agaric, ESR, vanadium

Abstract—Electron spin resonance shows that vanadium(IV) is present as the same compound in the skin, gills, volva and flesh of the fungus *Amanita muscaria*

It has been known for some time that the chemical composition of the mushroom *Amanita muscaria* ('fly agaric') is extraordinary [1] Apart from the unusual organic pigments (e g muscaflavin) and psychoactive materials (e g muscazone and muscimole) isolated from the fungus, the presence of vanadium was reported as early as 1931 [2] More recently, Bayer and Kneifel [3, 4] isolated a vanadyl complex called amavanadin after extraction of frozen mushrooms with methanol

In our studies of the reactions of α-amino acids with the vanadyl ion VO^{2+} (Gillard, R D, Costa Pessoa, J, Vilas Boas, L F and Lancashire, R J, unpublished results) we have used a number of techniques to aid in the characterization of the species produced One of these techniques is electron paramagnetic resonance (EPR, also known as electron spin resonance ESR) (preliminary results were presented [5] at a meeting in 1979) Using this technique it is possible to study segments of the mushroom directly

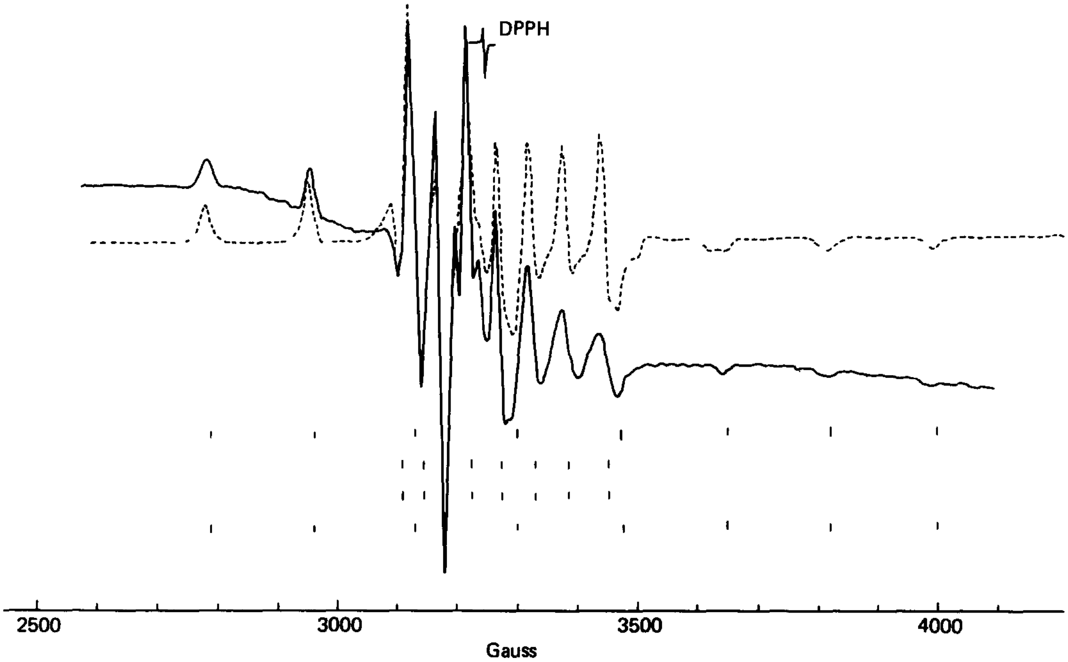

Fig 1 Figure shows a typical $^{51}V(IV)$ ESR spectrum from *Amanita muscaria* recorded at 77 K the spectrum shows well-resolved parallel and perpendicular hyperfine interactions A computer simulation based on the experimental parameters given in Table 1 is also shown as the dotted line DPPH (diphenylpicrylhydrazyl) was used as a field marker

Table 1 ESR parameters for vanadium-containing complex compounds

Source	Conditions	g_z	g_{xy}	A_z	A_{xy}
VO(L-ala)$_2$	pH 6 6	1 943	1 976	163	55
A muscaria	*	1 920	1 982	153	45
VO(serine)$_2$	pH 11 0	1 955	1 976	150	45
VO(cysteine)$_2$	pH 7 8	1 962	1 976	143	45

*Directly measured using a Varian E109 spectrometer on red skin, stipe, gills, volva (and this last repeated after a week was essentially unchanged)

without prior treatment and hence perhaps gain more insight into the mechanism of vanadium metabolism [6] Similar work on intact plant material may well be feasible with other paramagnetic species like copper(II)

We now wish to report that segments taken from a number of positions from an intact, fresh mushroom all give the same signal (Fig 1) (although intensities vary due to changes in concentration) and thus show that the same vanadyl complex is present in the red skin, the gills, the volva and the base As found previously [3, 4] the highest concentration is obtained in the bulbous base

Comparisons of the spectra and EPR parameters obtained for segments of the frozen mushroom to those of α-amino acid vanadyl complexes suggest a greater similarity of the chelating ligand to possible terdentate species such as L-cysteine or L-serine rather than to the simpler amino acids such as glycine or L-alanine (Table 1)

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DEPSIDONES AND FATTY ACIDS OF *PARMELIA STYGIA*

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Key Word Index—*Parmelia stygia*, Parmeliaceae, lichen, depsidones, fatty acid, norcaperatic acid

Abstract—One Russian sample of the lichen *Parmelia stygia* has yielded fumarprotocetraric acid, while a second contained the same compound accompanied by colensoinic, lobaric, caperatic and norcaperatic acids

Parmelia stygia (L) Ach is a widespread lichen of alpine zones and highland rocky deserts Three chemical dissimilar strains of this lichen are known (a) a fumarprotocetraric acid strain, (b) an acid-deficient strain, and (c) a caperatic acid strain [1] Strains 'a' and 'b' are generally abundant in arctic regions, while 'c' has only been found so far in Japan and Alaska We have investigated two samples of *P stygia* sample 1 was collected in June 1977 in the Magadan district (lat 63°N, 600 m on dazite), and sample 2 in July 1981 in the Khabarovsk district (lat 55°N, 2200 m on ryolite)

The TLC of an acetone extract of the first sample (3 2 % dry wt) showed fumarprotocetraric acid to be the main component, this was identified by direct comparison with an authentic sample Preparative TLC of an acetone extract of the second sample (11 4 % dry wt) in benzene–acetone (7 3) on silica gel resulted in five components

1—$C_{25}H_{30}O_7$ (430 mg), mp 173–174°, $[M]^+$ 442, methyl ester, mp 54–55°, $[M]^+$ 456

2—$C_{25}H_{28}O_8$ (270 mg), mp 195–197°, $[M]^+$ 456, methyl ester, mp 120–121°, $[M]^+$ 470

3—$C_{21}H_{38}O_7$ (423 mg), mp 132–133°, $[\alpha]_D^{20}$ − 24 5° (*c* 0 2, $CHCl_3$), IR ν_{max}^{KBr} cm^{-1} 1736, 1687, dimethoxy derivative (diazomethane) mp 55°, $[M]^+$ 430

4—$C_{20}H_{36}O_7$ (152 mg), mp 137–139°, $[\alpha]_D^{23}$ − 16 0 (*c* 0 19, EtOH), IR ν_{max}^{KBr} cm^{-1} 1706 (br), trimethyl derivative (diazomethane), mp 55–56°, $[M]^+$ 430

5—$C_{22}H_{16}O_{12}$ (2 6 g), mp 250–260° (dec)

On the basis of IR, ^{1}H NMR and MS spectral data for the