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HYDROXYLAGOPODIN B, A SESQUITERPENOID QUINONE FROM A MUTANT STRAIN OF *COPRINUS MACRORHIZUS* VAR. *MICROSPORUS*

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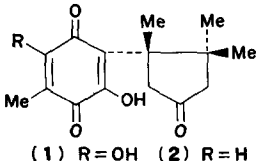
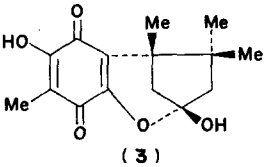
Key Word Index—*Coprinus macrorhizus* var. *microsporus*; Basidiomycetes; mushroom; isolation; characterization, sesquiterpenoid quinone; hydroxylagopodin B.

Plant. Coprinus macrorhizus var. *microsporus. Source.* Dr Philip G. Miles, Biology Department, SUNY at Buffalo.

Present work. A single gene mutant of the basidiomycete *Coprinus macrorhizus* var. *microsporus* (5074) excretes into the liquid culture medium an intense violet pigment which represents a series of possibly related compounds [1]. One of these has now been characterized as hydroxylagopodin B(**1**) which is clearly related to lagopodin B (**2**) [2], isolated from *Coprinus lagopus.*



(**1**) R=OH (**2**) R=H



(**3**)

The pigments were isolated by EtOAc extraction of the acidified filtered spent medium. The extract was evaporated *in vacuo* to dryness, the tarry residue redissolved in EtOAc and the pigments extracted into 0·1 M $NaHCO_3$. The bicarbonate phase was acidified (pH ~ 3) and extracted with C_6H_6. Following evaporation of this extract to near dryness, the residue was dissolved in 2% MeOH–$CHCl_3$ and separated on silica gel; (**1**) was eluted with 2% MeOH–$CHCl_3$ as the second purple band which yielded red–orange rhombic platelets (from C_6H_6–heptane), m.p. 184–186°. Yield: 3·5 mg/l of culture medium. Alkaline aqueous solutions of (**1**) were violet. Its solutions are decolorized by $NaBH_4$ and the color restored on aeration after the addition of $NaHCO_3$. UV λ_{max} (EtOH) 212, 307 and 351 nm is consistent with a 2,5 dihydroxy-3-6-dialkylbenzoquinone, e.g. helicobasidine [3].

The IR spectrum (KBr) showed OH at 3500 and 3385 cm^{-1}, characteristic (hydroxyquinone) CO absorptions at 1650 and 1627 cm^{-1}, and alkane C–H stretching bands in the region of 2900–3000 cm^{-1}. The cyclopentanone carbonyl band, which should appear at ~ 1750 cm^{-1}, was not present. This suggests that crystalline hydroxylagopodin B exists as a hemiketal structure (**3**) [3].

Hydroxylagopodin B has a molecular formula, $C_{15}H_{18}O_5$(M^+ 278), as determined by high resolution MS. Major ions in MS: *m/e* 280 (5·7), 278 (56·5), 221 (78·3), 194 (100), 166 (23·6). The strong M + 2 peak is observed which is typical of *p*-benzoquinones [3]. The fragmentation pattern confirms that hydroxylagopodin B is related to lagopodin B, the most abundant ion (100%) in the latter being at *m/e* 178. The ion *m/e* 166 arises from the expected elimination of an acetylene fragment from the benzoquinone ring.

Biological significance. The lagopodins have some antibiotic activity. No test of the antibiotic properties of hydroxylagopodin B was made.

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REFERENCES

1. Bottom, C. B. and Siehr, D. J. (1972) *The pigments of a mutant of* Coprinus macrorhizus microsporus, presented at 8th Midwest Regional ACS Meeting, Columbia, Missouri.
2. Bollinger, P. (1965) Über die Konstitution und Konfiguration der Lagopodine A, B, und C, Ph.D. Thesis, ETH, Zurich.
3. Thomson, R. H. (1971) *Naturally Occurring Quinones*, Academic Press.