

Occurrence of Bisnoryangonin in *Pholiota squarroso-adiposa*

Keyphrases □ *Pholiota squarroso-adiposa*—isolation, identification of bisnoryangonin □ Bisnoryangonin— isolation, identification from *Pholiota squarroso-adiposa* □ TLC— isolation □ Mass spectroscopy— identification

Sir:

Mycologic knowledge of the genus *Pholiota* (Fr.) Kummer is reasonably adequate (1), but there is a paucity of information on the chemical composition and pharmacologic properties of members of the genus *sensu* Smith and Hesler. Reports of the deadly poisonous *P. autumnalis* Pk. (2, 3) and related species (4, 5) refer taxonomically to amanita toxin-containing *Galerina* species (6–8), and the purportedly hallucinogenic styrylpyrone-containing *P. spectabilis* (Fr.) Gill. (9–12) is currently assigned to the genus *Gymnopilus* by mycologists (1, 13).

The primary importance of *Pholiota* species is acknowledged generally to be ecologic and related to their destructive impact as forest parasites and their valuable contribution to slash disposal (1); development of the genus appears to have centered on physiologic specialization involving the use of wood components as nutrients. Preliminary information available in the authors' laboratory indicated that phenylpropanoid constituents of the type which could arise during the degradation of lignin were biosynthetic precursors of fungal styrylpyrones. *P. squarroso-adiposa* Lange, a yellowish-brown lignicolous species encountered in the Pacific Northwest, was selected for investigation to determine if there was any indication for the presence of a styrylpyrone-producing capability in the genus.

Carpophores of the mushroom¹ were dried in a forced-air oven at 48°. Three grams of powdered material was extracted by shaking with 150 ml. of methanol. The concentrated methanolic extract was examined in three TLC systems [silica gel G adsorbent and methyl formate-*n*-hexane-formic acid (100:50:1); polyamide adsorbent and 95% ethanol; Eastman cellulose 6064 plates and *n*-butanol-glacial acetic acid-water (4:1:1)] which had been found to be satisfactory for detecting styrylpyrones in extracts of *Gymnopilus* species (14); a *p*-dimethylaminobenzaldehyde reagent was used for visualization. Chromophoric and chromatographic properties of the major component in the extract were indistinguishable from those of bisnoryangonin [4-hydroxy-6-(4-hydroxystyryl)-2-pyrone]. The concentration of bisnoryangonin was estimated to be approximately 18 mg./g. of dried mushroom based on a visual, semi-quantitative evaluation of chromatograms spotted with gradient quantities of the extract and reference material (14). Chromatograms containing larger quantities of the extract revealed a minor constituent with

properties corresponding to those of hispidin; the apparent low concentration of the compound in the dried mushroom (estimated 0.4 mg./g. or less), the presence of other impurities in the extract, and the limited availability of plant material precluded further purification and verification of the identity of this minor constituent.

Purification of the major pigment in the extract was achieved with a dry-column chromatographic procedure [acid-washed silica gel adsorbent (activity grade II) and the TLC methyl formate-*n*-hexane-formic acid solvent mixture] which had been developed for styrylpyrone-containing extracts from *Gymnopilus* species (14). Chromatographically pure material was subjected to high-resolution mass spectroscopy². The parent ion (*m/e* 230.0579), the next most abundant peak (*m/e* 147.0446), and the pattern of other prominent fragmentation peaks (*m/e* 213, 202, 188, 187, 161, and 160) in the mass spectrum of this pigment were in agreement with the known spectrum of bisnoryangonin (14).

The identification of bisnoryangonin in extracts from *P. squarroso-adiposa* represents the first reported detection of a styrylpyrone constituent in the genus *Pholiota* and the first reported occurrence of bisnoryangonin outside the genus *Gymnopilus*.

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¹ Collected near Friday Harbor, Wash., November 18, 1966. A specimen was retained for herbarium reference.

² Picker-AEI MS-9 mass spectrometer, Picker Nuclear Division, White Plains, N. Y.