

ABSENCE OF PSILOCYBIN IN SPECIES OF FUNGI PREVIOUSLY REPORTED  
TO CONTAIN PSILOCYBIN AND RELATED TRYPTAMINE DERIVATIVES

T. STIJVE\* &amp; Th. W. KUYPER\*\*

Seven taxa of agarics reported in literature to contain psilocybin (viz. *Psathyrella candolleana*, *Gymnopilus spectabilis*, *G. fulgens*, *Hygrocybe psittacina* var. *psittacina* and var. *californica*, *Rickenella fibula*, *R. swartzii*) have been analysed for psilocybin and related tryptamines with negative results.

The presence of psilocybin, psilocin and/or baeocystin has been well established in the following families of gill-fungi: Strophariaceae (mainly *Psilocybe* (Fr.) Kumm.; see Guzmán, 1983, for a review), Coprinaceae (*Panaeolus* (Fr.) Quél.; Ola'h, 1969; Stijve & Kuyper, 1985), Bolbitiaceae (*Conocybe* Fay.; Benedict & al., 1962), Pluteaceae (*Pluteus* Fr.; Saupe, 1981; Stijve & Bonnard, 1986), and Cortinariaceae (*Inocybe* (Fr.) Fr.; Stijve & al., 1985; Gartz & Drewitz, 1985).

There are (unconfirmed) reports on the occurrence of psilocybin in members of the genus *Gymnopilus* P. Karst. (Cortinariaceae; Hatfield & al., 1978; Ott & Bigwood, 1978), *Psathyrella* (Fr.) Quél. (Coprinaceae) and *Agrocybe* Fay. (Bolbitiaceae; Koike & al., 1981). Recently, Gartz (1986) reported the presence of significant quantities of the hallucinogen in *Rickenella fibula* (Bull.: Fr.) Raithelhuber and *R. swartzii* (Fr.) Kuyp. (Tricholomataceae), *Hygrocybe psittacina* (Schaeff.: Fr.) Wünsche (Hygrophoraceae), *Inocybe calamistrata* (Fr.: Fr.) Gillet, and *Psathyrella candolleana* (Fr.: Fr.) R. Maire. A further collection of that latter species was found to be exempt of psilocybin, however (Gartz, pers. comm.).

The present authors were rather surprised by these findings, because they had already analysed some of these species with negative results. In order to establish the absence or presence of psilocybin in the said fungi beyond reasonable doubt, recent collections of various origin, in some cases from both sides of the Atlantic Ocean, were analysed.

## MATERIALS AND METHODS

Specimens of the species of interest were gathered in Switzerland, the Netherlands, Canada (Ottawa), and several sites in the USA. The material was dried and analysed as described previously (Stijve & al., 1984).

\* Central Quality Assurance Laboratory of Nestec Ltd., Avenue Nestlé 55, 1800 Vevey, Switzerland.

\*\* Biologisch Station Wijster, Landbouwniversiteit Wageningen, Kampsweg 27, 9418 PD Wijster (Dr.), Netherlands. (Communication 342, Biologisch Station Wijster.)

## RESULTS AND DISCUSSION

Psilocybin, baeocystin, and related tryptamines were found to be absent in the collections of all species listed in Table I.

The limit of detection was 0.005 percent on dry weight. Besides tryptophan, a widely occurring amino acid, the only tryptamine derivative encountered was 5-hydroxytryptophan in the three collections of *Rickenella fibula*. This compound may probably be considered a waste product of the species' ammonia metabolism. 5-hydroxytryptophan is also widely encountered in Panaeoloideae (Stijve, 1985), where it is an intermediary in the biosynthesis of serotonin which may have a similar function.

*Rickenella swartzii* on the other hand does not contain any 5-OH-tryptophan, yielding additional chemotaxonomic support for the autonomy of both species, which also differ in colour of the basidiocarp and spore-form. Contrary to the opinion of Gartz (l.c.), this situation cannot be compared with bluing and non-bluing variants of *Psilocybe semilanceata*.

Our analytical results contradict those reported by Koike & al. (1981) and by Gartz (1986).

The reason for this is hard to explain, especially since the analytical methodology of the Japanese scientists includes several confirmatory procedures. However, they describe a screening method by HPLC with UV detection at 220 nm, which may not be sufficiently selective. Using their technique on *Psathyrella candolleana*, we found indeed absorbing material with about the same retention time as psilocybin, but the result could not be confirmed by thin-layer chromatography.

Table I. Species analysed for psilocybin and related tryptamines with negative results

Species	N	Origin
<i>Psathyrella candolleana</i>	5	Switzerland, Washington DC (USA), and Ottawa (Canada)
<i>Gymnopilus spectabilis</i>	3	Switzerland, Netherlands, and USA
<i>Gymnopilus fulgens</i>	1	Netherlands
<i>Hygrocybe psittacina</i> var. <i>psittacina</i>	5	USA, Switzerland
<i>H. psittacina</i> var. <i>californica</i> (Hesl. & Smith)	1	USA
<i>Rickenella fibula</i>	3	Netherlands, Switzerland
<i>Rickenella swartzii</i>	1	Netherlands

On the other hand, our negative result for *Gymnopilus spectabilis* is in agreement with that of Koike & al. who found only traces of psilocybin in *G. liquiritiae*, a species not available for analysis in this laboratory.

Gartz's finding of psilocybin in the 5 mentioned species, which we found to be exempt of the compound, is rather puzzling. It is worth noting that the author did not report exact quantitative results, but only mentioned that the fungi contain about 0.05 percent on dry matter or even less. It is also remarkable that he failed to note tryptophan in several collections studied.

Gartz's concentration range is uncomfortably close to the limit of detection of his method. Indeed, TLC of crude extracts on commercially available, pre-coated silica gel sheets using Ehrlich reagent for detection will do for psilocybin concentrations of 0.05–0.5 percent. Detection of lower levels is, however, hampered by the need for higher sample loading and the limited selectivity of the chromogenic reagent, since much extraneous material may turn up as Ehrlich-positive spots. Under such conditions there may indeed be a risk of false-positive results.

The higher sensitivity (0.005%), reported in this paper was attained by using different layers (silica gel and cellulose), and the more sensitive and selective pDMCA-reagent (Stijve & al., 1984).

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