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OCCURRENCE OF PSILOCYBIN, PSILOCIN AND BAEOCYSTIN IN GYMNOPILUS PURPURATUS

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Analysis of *Gymnopilus purpuratus* from two localities in the G.D.R. revealed the presence of psilocybin, psilocin and low concentrations of baeocystin. Psilocybin levels varied from 0.07% up to 0.33% of dry weight of the bluing basidiocarps. The psilocin content was high and reached 0.31% of dry weight. The highest concentrations of the alkaloids were found in the smallest basidiocarps. High levels of psilocybin were found to be correlated with high levels of psilocin and baeocystin. Caps contained more baeocystin than stems; the concentration of psilocin was highest in the stems. Other tryptamines, muscarin and urea were absent from this hallucinogenic species.

Gymnopilus purpuratus (Cooke & Mass.) Sing. is an agaric from the austral floral zone (Singer, 1969, 1975). But since 1983 this species has been observed on heaps of mixtures of pig dung and wood chips in the district Rostock, northern G.D.R. (Kreisel & Lindequist, 1988).

It seems that this species was introduced with grain from Argentina used for forage in pig-breeding during the last years. Various higher plants from South America have also been found in woods with pig-breeding in this district (Müller, pers. comm.).

Recently, the qualitative detection of the indole alkaloid psilocybin in extracts of *G. purpuratus* from the G.D.R. has been described by Kreisel & Lindequist (1988). However, quantitative studies or analyses of psilocybin or other indole alkaloids in this species have not been published.

In literature several other species of *Gymnopilus* are mentioned as to contain psilocybin (Hatfield & al., 1978; Koike & al., 1981).

In continuation of studies in which we reported the quantitative detection of the alkaloids psilocybin, psilocin, and baeocystin in various agarics (Gartz, 1987a; Semerdžieva & al., 1986), in this paper the analysis of the indolic constituents of *G. purpuratus* is described.

MATERIALS AND METHODS

Basidiocarps of *G. purpuratus* were gathered in the northern G.D.R. Voucher specimens have been deposited in the herbarium of the Karl-Marx-University of Leipzig (LZ) and in the Rijksherbarium, Leiden.

Twenty basidiocarps from Klockenhagen (30.8.88-locality 1) and six from Tressentin (20.9.87-locality 2) were dried at room temperature. Possibly present residual water was

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removed from the mushrooms by freeze drying. The extraction procedure (Stijve & al., 1985) and the qualitative and quantitative analysis of the indole alkaloids by using HPLC and TLC have been described in earlier papers (Gartz, 1985a, b; 1987a, b; Semerdžieva & al., 1986). The stem and cap of some mushrooms were analysed separately. All extracts were also analysed by TLC for muscarin (Gartz, 1986).

Results and discussion

Psilocybin and its precursor baeocystin were found in every basidiocarp from both localities (Table 1 and 2). The identity of the compounds was confirmed by TLC in three different systems and by HPLC.

The highest concentrations were found in the smallest basidiocarps, as earlier was the case in *Psilocybe cubensis* (Earle) Sing. grown in controlled cultures (Gartz, 1987a). The psilocybin content of the smaller basidiocarps of *G. purpuratus* was in the same order of magnitude as that found in basidiocarps of *Inocybe aeruginascens* Babos (Gartz, 1987b). In *G. purpuratus* psilocybin was found to be accompanied by only slight amounts of baeocystin. *Inocybe aeruginascens* contains much higher concentrations of this substance (Gartz, 1987b).

High concentrations of psilocin were detected in all extracts of *G. purpuratus* from locality 1 (Table 1). Such substantial amounts of psilocin have not been found in any other European agaric (Gartz, 1987b; Semerdžieva & al., 1986; Stijve & Kuijper, 1985; Stijve & al., 1985; Stijve & Bonnard, 1986). The caps of the basidiocarps contained more baeocystin than the stems, but the levels of psilocin were highest in the latter (Table 1). Basidiocarps with the highest psilocybin levels also contained the largest amounts of psilocin and baeocystin.

It seems that the levels of the unstable compound (Repke & al., 1977) psilocin decrease appreciably during storage. Analysis of basidiocarps from locality 2 revealed only slight amounts of this alkaloid one year after collection (Table 2). The psilocybin concentrations were found in the same order of magnitude in the mushrooms from both collections (Table 1 and 2). This is in agreement with the observation that psilocybin was the most stable compound of the tryptamines reported in species of *Psilocybe, Panaeolus,* and *Pluteus* (Stijve & al., 1985; Stijve & Kuijper, 1985).

Gymnopilus purpuratus is characterized by a typical blue colouration caused by handling of the mushrooms. Mature basidiocarps often possess blue flecks on the pileus and a bluish stipe. This colouration has been observed also in many other psilocybin-containing mushrooms (Gartz, 1987a; Stijve & al., 1985).

It is interesting to note that *G. purpuratus* was found to be exempt of muscarin, just as the hallucinogenic species of *Inocybe* studied so far (Gartz, 1986; Stijve & al., 1985). Urea, tryptophan, tryptamin, serotonin, and its precursor 5OH-tryptophan as well as the not yet identified indole derivative aeruginascin (Gartz, 1987b) were also found to be absent from both collections of *G. purpuratus*.

The typical brownish dye of the mushroom gave a yellow spot during TLC on silica gel. No definite conclusions can be drawn about the pathway of the biochemical synthesis of psilocybin in *G. purpuratus*. The presence of high concentrations of psilocin suggests that

methylation mainly preceeds phosphorylation, implying the following reactions (Repke & al., 1977): tryptophan →tryptamin→4-hydroxytryptamin→psilocin→psilocybin.

Gymnopilus purpuratus is the first psilocybin-containing *Gymnopilus* species collected in Europe.

Table 1: Amount of indole alkaloids in dried fruit bodies (fb) of *Gymnopilus purpuratus* from locality 1.

Sample	dry weight of the mushroom (g)	part of the mushroom	psilocybin (% dry weight)	psilocin (% dry weight)	baeocystin (% dry weight)
1	0.202	fb	0.29	0.28	0.05
2	0.208	fb	0.31	0.29	0.04
3	0.209	fb	0.21	0.20	0.03
4	0.211	fb	0.28	0.31	0.04
5	0.220	fb	0.33	0.28	0.05
6	0.418	fb	0.15	0.12	0.02
7	0.581	fb	0.15	0.21	0.02
8	0.602	fb	0.18	0.11	0.02
9	0.633	fb	0.18	0.19	0.01
10	0.695	fb	0.14	0.17	0.02
11	0.762	fb	0.15	0.18	0.02
12	0.821	fb	0.10	0.18	0.01
13	1.180	fb	0.10	0.09	0.01
14	1.188	fb	0.08	0.10	0.01
15	1.197	fb	0.11	0.11	0.02
16	1.512	fb	0.09	0.10	0.005
17	1.712	fb	0.07	0.05	0.01
18	2.201	cap	0.21	0.04	0.04
19		stem	0.03	0.15	0.005
20	3.713	cap	0.12	0.03	0.03
21		stem	0.03	0.18	0.01
22	4.075	cap	0.05	0.06	0.03
23		stem	0.13	0.13	0.01

Table 2: Concentration of psilocybin, psilocin and baeocystin in *Gymnopilus purpuratus* from locality 2.

Sample	dry weight of the mushroom (g)	part of the mushroom	psilocybin (% dry weight)	psilocin (% dry weight)	baeocystin (% dry weight)
1	0.281	fb	0.32	0.03	0.03
2	0.350	fb	0.21	0.02	0.02
3	0.821	fb	0.18	0.04	0.02
4	1.234	fb	0.13	0.01	0.02
5	1.932	fb	0.12	0.02	0.01
6	2.467	cap	0.14	0.01	0.03
7		stem	0.04	0.05	0.005

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