calc. for $C_{30}H_{46}O_4$: 470.340), 452 (19) (M-H_2O), 424 (9) (452 - CO), 409 (10) (424 - CH_3), 368 (10), 246 (18), 205 (58), 187 (51), 81 (74), 55 (100); addition of diazomethane afforded the corresponding methylester; ^{1}H-NMR ($CDCl_3$, δ ppm): 0.92, 0.95, 0.98, 1.02, 1.07 and 3.67 (3H each, s), 4.97 and 4.92 (each 1H, br, s), 4.12 (2H, br, s), 2.88 (1H, ddd, J = 11, 11, 5), 2.49 (1H, ddd, J = 17, 10, 9), 2.40 (1H, ddd, J = 17, 7, 4);

$$[\alpha]_{24°}^{\lambda} = \frac{589\ \ 578\ \ 546\ \ 436\ \text{nm}}{+10 +11 +14 +18} \quad (CHCl_3;\ c = 0.64)$$

3β-[2-Methylbutyryloxy]-preeupatundin-1α,14-epoxide (**2**): Colourless oil; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3600 (OH), 1765 (γ-lactone), 1730 (CO_2R); MS: 260.105 (2) (M-RCO_2H) (calc. for $C_{15}H_{16}O_4$: 260.105), 242 (6) (260 - H_2O), 85 (32) ($C_4H_9CO^+$), 57 (100) (85 - CO); ^{1}H-NMR ($CDCl_3$, δ ppm): 4.84 (1H, br, d, J = 6, 2-H), 5.73 (1H, br, s, 3-H), 2.61 (1H, br, t, J = 10, 5-H), 4.69 (1H, dd, J = 10 and 9, 6-H), 3.18 (1H, dddd, J = 9, 4, 3, 3, 7-H), 5.51 (1H, ddd, J = 8, 8, 4, 8-H), 2.91 (1H, ddd, J = 15, 9, 1.5, 9α-H), 1.97 (1H, dd, J = 15, 9, 9β-H), 6.35 (1H, d, J = 3.5, 13-H), 5.54 (1H, d, J = 3, 13′-H), 2.77 (1H, d, J = 5, 14-H), 2.71 (1H, dd, J = 5, 1.5, 14′-H), 2.00 (3H, br, s, 15-H), 2.30 (1H, tq, J = 7, 7, 2′-H), 0.83 (3H, t, J = 7, 4′-H), 1.04 (3H, d, J = 7, 5′-H),

$$[\alpha]_{24°}^{\lambda} = \frac{589\ \ 578\ \ 546\ \ 436\ \text{nm}}{-32 -32 -36 -60} \quad (CHCl_3;\ c = 0.2)$$

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Psilocybin in Finnish *Psilocybe semilanceata*

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Abstract: The use of a hallucinogenic mushroom, *Psilocybe semilanceata*, has been occasionally reported in Finland, where the species is widely distributed. We have determined, by HPLC, the content of psilocybin and psilocin in *P. semilanceata* samples collected from different parts of Finland; the psilocybin content was found to be high (0.62–2.37 %, mean 1.42 % of dry weight), some samples also contained low concentrations (0.01–0.02 % dry weight) of psilocin.

Introduction

The traditional use of psilocybin-containing mushrooms in Central America was the focus of intense scientific interest in the 1950s. The psychoactive effects of psilocybin and its active metabolite, psilocin, are similar to those of LSD. It is now known that psilocybin is present not only in some tropical species, but also in some mushroom species in different parts of the world (1), and their ingestion in Western Europe is an area of increasing toxicological significance (2, 3). Six years ago the occurrence of a psilocybin-containing species, *Psilocybe semilanceata* (Fr. ex Secr.) Kummer, was reported (4) in Scandinavia. Chemical and botanical work (5) on Norwegian *P. semilanceata* showed it to be widely distributed and a potent hallucinogenic mushroom. Since 1981, the use of psilocybin-containing mushrooms has been recorded in some narcotic trials in Finland and at least one hospital case has been reported (6). Therefore we have determined, using a high performance liquid chromatographic method, the psilocybin and psilocin contents of *P. semilanceata* mushrooms picked from various localities in Finland.

Material and Methods

Figure 1 shows the localities where *P. semilanceata* has been found and where samples were collected for the present study. Immediately after harvesting (August-October 1982) the samples were dried overnight at 50° C and then stored in airtight bags at −20° C until analysed. The identities of the dried mushroom samples were confirmed by the professional mycologist of our group (E. O.).

The psilocybin and psilocin contents were analyzed with high performance liquid chromatography (HPLC) as described by Christiansen et al. (7) with minor modifications. Each mushroom was analyzed separately. The dried mushrooms were weighed and ground to powder which was extracted twice with a total of 5.00 ml of 10 % 1 N ammonium nitrate in methanol. The HPLC system: pump: Varian Model 5000, injector: Rheodyne Model 7125 (20 µl external loop), stationary phase: Hibar® 250-4 (E. Merck, Darmstadt) prepacked with 5 µm LiChrosorb®, mobile phase: methanol–water–1N NH_4NO_3 (220 : 70 : 10) buffered to pH 9.6 with 2 N ammonia, flow rate 1 ml/min, detector: Varian Vari-Chrom®, wavelength 267 nm, quantitation: peak areas monitored with a Shimadzu Chromatopac C-R18 data processor. The calibration graphs from pure psilocybin and psilocin standards (Sandoz, Basle) showed excellent linearity (r 0.9996 and 0.9992, respectively).

Results and Discussion

The recorded distribution of *P. semilanceata* in Finland (Fig. 1) suggests that this mushroom can be found in all parts of the country. No clear difference in frequency seemed to occur between the coastal and inland regions. The analyzed samples were found among grass in pastures, untrimmed and trimmed lawns, on decaying straw etc. from 29th August to 15th November, though the main season in Finland seems to be in September. The phenology of the studied collections varies from the 12th July to the 15th November (in the years 1867–1983). The mean dry weight (± S. D.) of a random sample (100 specimens) of Finnish *P. se-*

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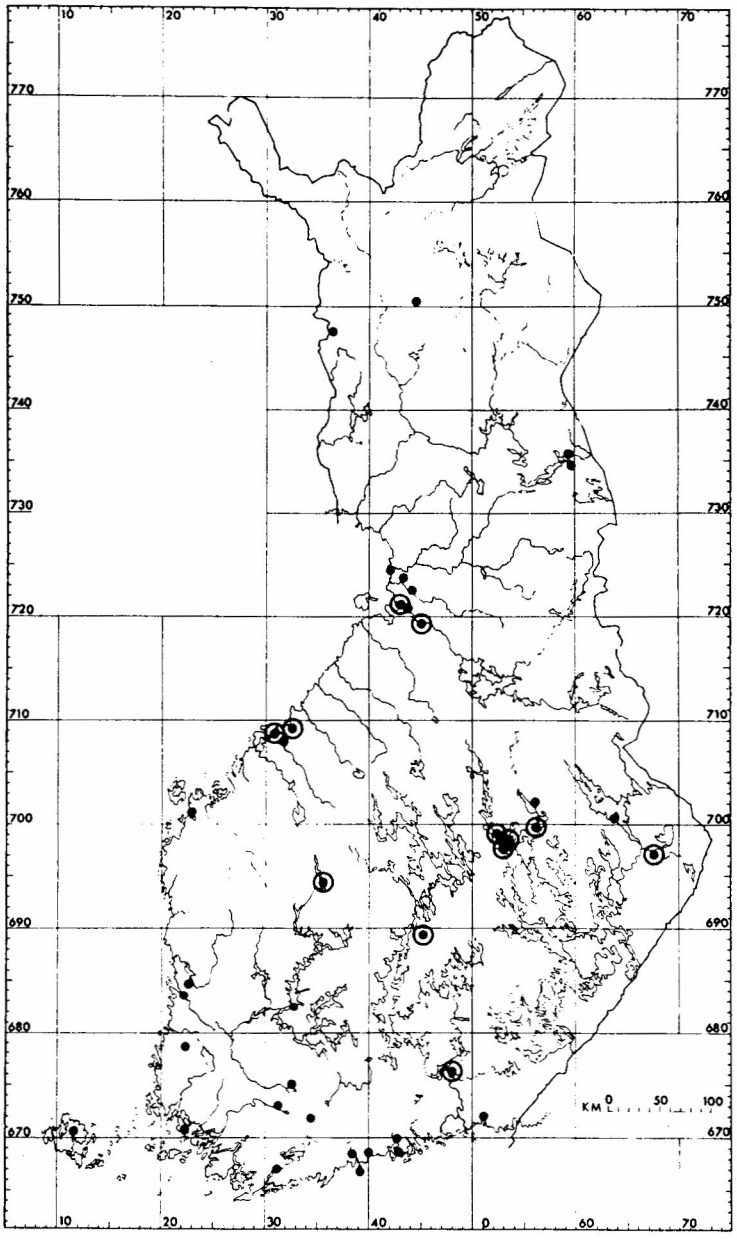

Fig. 1. Distribution of *Psilocybe semilanceata* (Fr. ex Secr.) Kumm. according to the collections made by the authors and the material preserved in the Finnish botanical museums (black dots). The ringed dots indicate the places of samples analyzed in the present study.

milanceata was 34.30 ± 18.64 mg. For the analyses, one mushroom of medium size, one of the smallest and one of the largest were selected from each location. The average weight loss during the drying procedure was 90 %.

The liquid chromatograms showed typically three peaks, one corresponding to psilocybin (rentention volume 6.8 ml), and another (usually very small) psilocin (r.v. 4.7 ml). The third one (r.v. 5.7 ml) remained unidentified but is possibly baeocystein (8).

Psilocin concentrations did not exceed 0.02 % of dry weight and were detectable only in some samples (detection limit about 0.005 %). Psilocybin concentrations did not seem to correlate with the date of collection or the geographical location, and the correlation with the mushroom size was weaker than that described from Norwegian *P. semilanceata* (5). The absolute amount of psilocybin, however, increased with the mushroom size (Table I).

Table I. Psilocybin contents and concentrations in different weight groups of Finnish *Psilocybe semilanceata* (mean ± S.D.)

Dry weight mg	Content mg	Concentration % of dry weight
up to 20	0.27 ± 0.10	1.63 ± 0.42
21–40	0.38 ± 0.07	1.45 ± 0.33
41–60	0.73 ± 0.20	1.43 ± 0.26
over 60	1.20 ± 0.43	1.23 ± 0.30
Mean 49.6 ± 36.9	0.64 ± 0.40	1.42 ± 0.36

The psilocybin concentration in the Finnish *P. semilanceata* varied from 0.62 % to 2.37 % (mean 1.42 %) and values of two larger pooled unselected samples were 1.68 and 1.53 % of dry weight (i.e. more than 1 mg/g of fresh mushroom). These values are among the highest described in any mushrooms.

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