Supplementary information:

SI-1: Document describing all recognized species of *Psilocybe* before and after 2006 with specimens only known from type collections highlighted. *Psilocybe* s.s. are colored green, those recognized as *Deconica* as red, and those found to be other taxa in purple. Here 141 unique taxonomic names are recognized as *Psilocybe* s.s. However, with future molecular and phylogenetic studies this number is likely to change, with many specimens currently in need of phylogenetic analysis, as well as taxonomic revision.

Supplementary Figures:

S1: Phylogenetic ITS rDNA tree using NCBI and UNITE sequences for *Psilocybe.*

S2: Chemical stack plots and chemical curve formulas.

S3: PCA of chemical factors from cultivated samples.

S4: PLS-DA analysis of cultivated samples.

Table S1: Table of chemical studies and methods of accepted *Psilocybe* spp.

Table S2: Voucher table for all generated ITS barcodes.

Table S3: Chemical control intensity values.

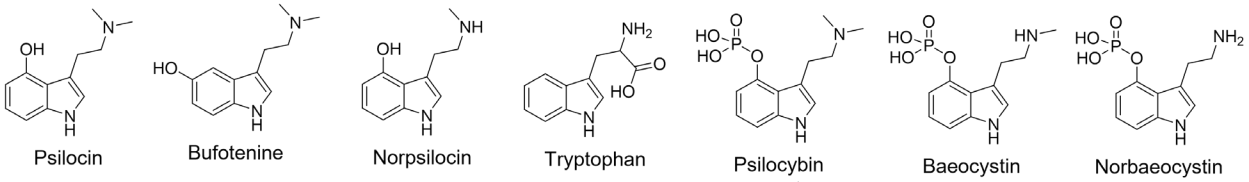
Table S4: Table of chemical factors and intensities.

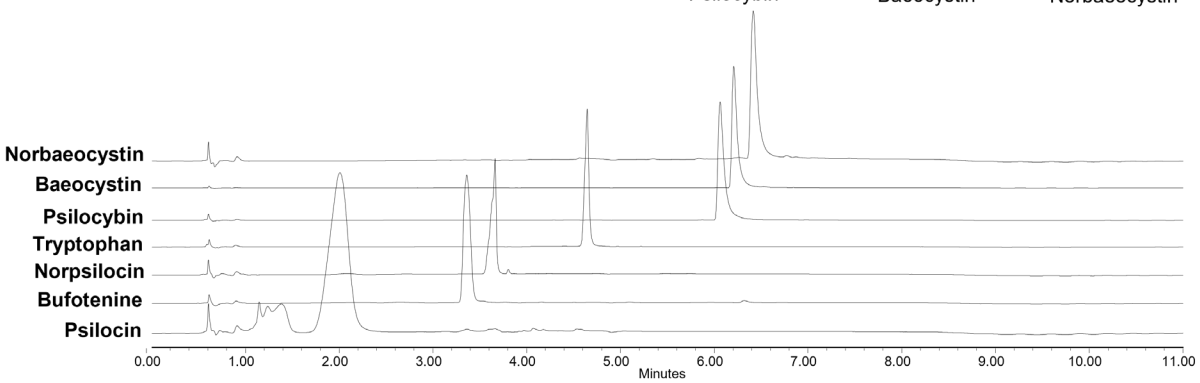
Table S5: Table of annotated compounds from Psi_6_cap

Supplementary figure 2:
Chemical standard trace plot along with all curve formulas and info
(Top) Chemical standard information for each standard including mass concentration, column retention time, compound mass, and slope formula from each standard curve.
(Bottom) chemical standard stack plot showing extracted ion content (EIC) for psilocybin, psilocin and its chemical intermediates produced during natural psilocybin production in *Psilocybe* species.

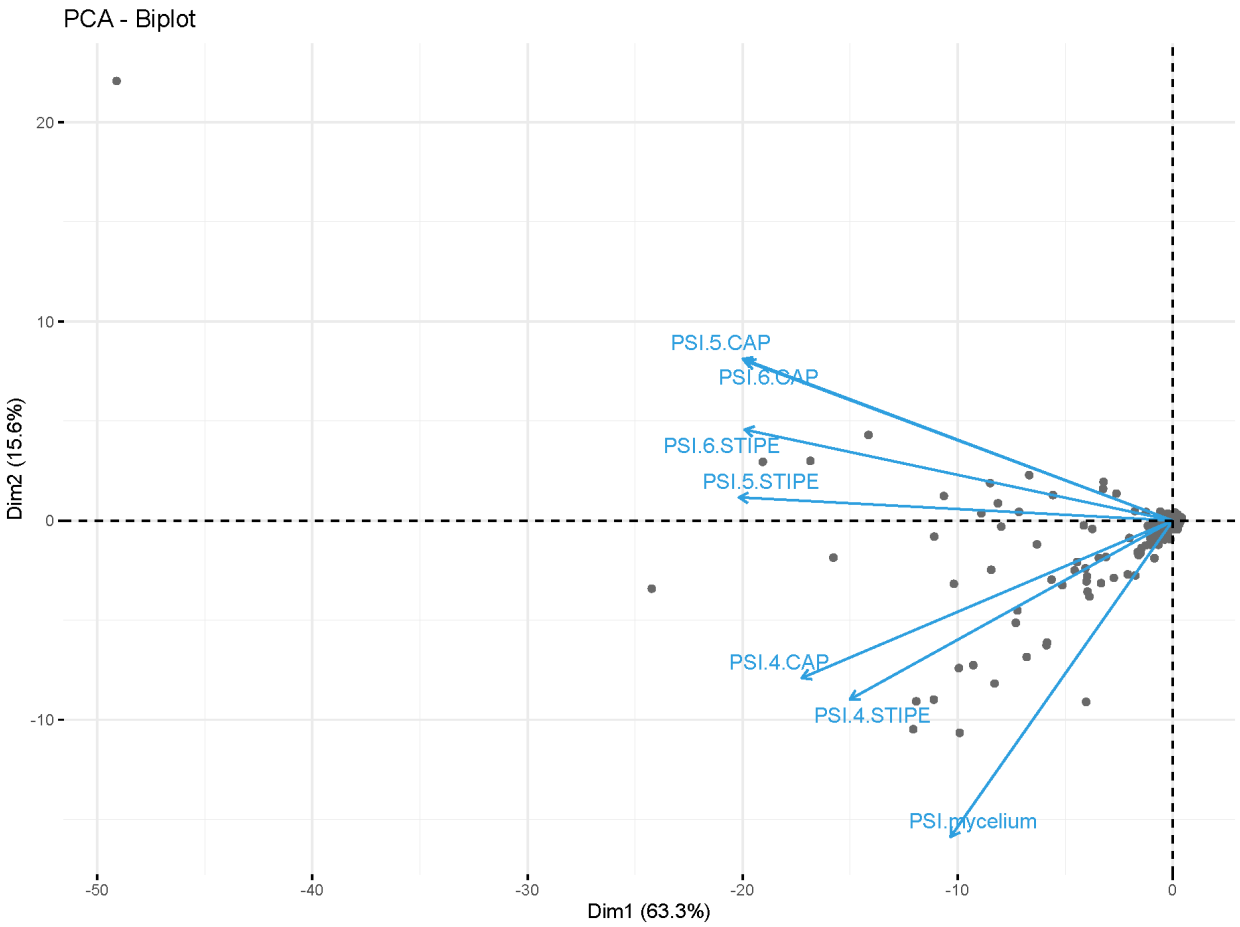
Chemical Standard Information

Standard	Retention Time	M/Z	Concentration	Curve Formula	R^2
Tryptophan	4.657'	205	100 ug/mL	y = 1E+06x	1.00
Psilocin	1.86'	205	100 ug/mL	y = 8E+06x	1.00
Psilocybin	6.087'	285	100 ug/mL	y = 1E+07x	0.99
Baeocystin	6.23'	271	100 ug/mL	y = 9E+06x	0.98
Norbaeocystin	6.412'	257	100 ug/mL	y = 1E+06x	1.00
Bufotenine	3.3'	205	100 ug/mL	y = 5E+06x	1.00
Norpsilocin	3.7'	191	100 ug/mL	y = 3E+06x	0.99

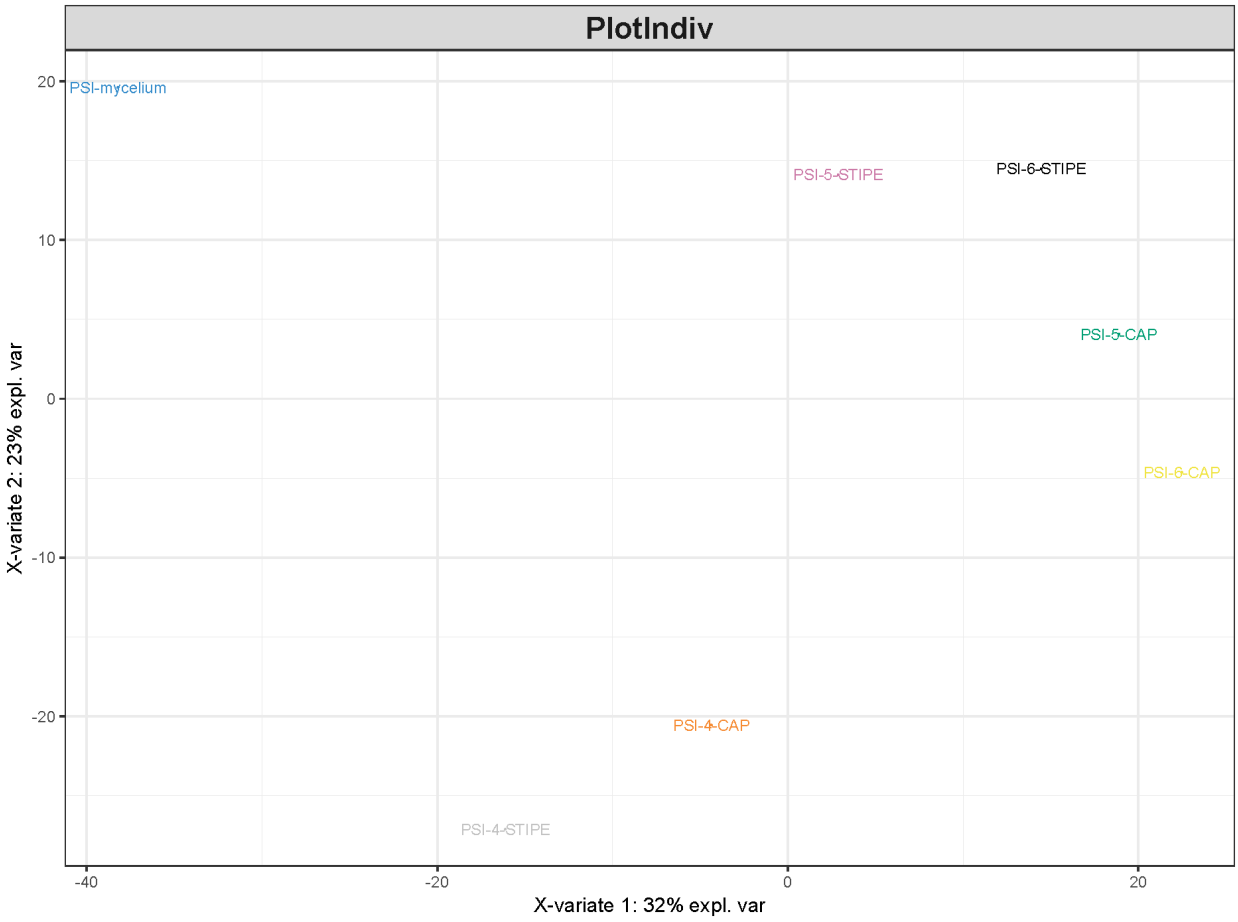




Supplementary figure 3:
Principal component analysis of the intensity for each identified chemical factor. Arrows indicate positive correlation based on samples. Most factors overlap between samples; however a general pattern of correlation occurs between caps and steps (Psi_5, and Psi_6), but separates between growing bins (Psi_4 vs Psi_5 and Psi_6)



Supplementary figure 4:
PLS-DA of samples based on chemical factors. A general pattern of correlation occurs between caps and steps (Psi_5, and Psi_6), but separates between growing bins (Psi_4 vs Psi_5 and Psi_6)



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