Psilocybin (systematic name: 3-[2-(dimethylamino)ethyl]-1H-indol-4-yl dihydrogen phosphate) is a zwitterionic tryptamine natural product found in numerous species of fungi known for their psychoactive properties. Following its structural elucidation and chemical synthesis in 1959, purified synthetic psilocybin has been evaluated in clinical trials, and has shown promise in its utility for the alleviation of suffering associated with various mental health disorders. In a recent process-scale crystallization investigation, three crystalline forms of psilocybin were repeatedly observed: Hydrate A, Polymorph A, and Polymorph B. The crystal structure for Hydrate A was previously solved by single crystal X-ray diffraction. This report presents new crystal structure solutions for the two anhydrates, Polymorph A and Polymorph B, based on Rietveld refinement using laboratory and synchrotron X-ray diffraction data and density functional theory (DFT) optimizations. Utilizing the three solved structures, investigation was conducted via Rietveld method (RM) based quantitative phase analysis (QPA) to estimate the contribution of the three different forms in powder X-ray diffraction (PXRD) patterns of different sources of bulk psilocybin produced between 1963 and 2021. Over the last 57 years, each of these samples quantitatively reflect one or more of the hydrate and anhydrate polymorphs. In addition to quantitatively evaluating the composition of each sample, this paper evaluates correlations between the crystal forms present, corresponding process methods, sample age, and storage conditions. Further, revision is recommended on characterizations in recently granted patents that include descriptions of crystalline psilocybin inappropriately reported as a single phase “isostructural variant”. Rietveld refinement demonstrated that the claimed material was composed of approximately 81% Polymorph A and 19% Polymorph B, both of which have been identified in historical samples. We show conclusively that all published data can be explained in terms of three well defined forms of psilocybin and that no additional forms are needed to explain the diffraction patterns.