The rice seedling blight fungus Rhizopus microsporus has an unusual symbiosis with a bacterium, Burkholderia rhizoxinica, which lives within the fungal cytosol and produces a potent phytotoxin that causes severe losses in agriculture. To gain insight into symbiosis factors we investigated the endosymbiont's exopolysaccharide (EPS), a secreted matrix that plays pivotal roles in mediating cell-environment interactions. By a combination of homo- and heteronuclear 2D NMR experiments, we elucidated a previously unknown EPS structure: a repeating tetrasaccharide unit bearing a nonstoichiometric acetyl group on a mannose residue. We also analyzed the EPS biosynthesis gene cluster and generated a targeted mutant to compare the phenotypes. Scanning electron microscope images revealed a reduced ability of the mutant to form extracellular polymers around cell aggregates. Phylogenetic analyses suggest that the symbiont's EPS genes are retained through evolutionary processes.