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Molecular Structure of Starch-Type Polysaccharides from Hericium ramosum and Hericium coralloides

Abstract. *Starch isolated from the fungi* Hericium ramosum *and* Hericium *coralloides differs from that of higher plants in that it consists only of short-chain amylose molecules (32 to 45 glucose units long).*

Despite the use of amyloidity as a taxonomic character in fungi since 1869 (*1*) the chemical structure of the "starch" has not been investigated. Among the Ascomycetes three major families of Pyrenomycetes are characterized by amyloid apical rings in the wall of the asci (*2*) and nine families of Discomycetes feature amyloidity in the ascus wall (*3*). Among the Basidiomycetes, amyloidity occurs in the spore walls of 35 genera of Agaricales (although in a relatively small number of species) and of at least 20 genera of the Aphyllophorales. Fungal starch differs from typical plant starch in three ways. (i) It is not produced in plastids; (ii) it is not found in granular form; and (iii) it is apparently a cell wall component (*4*). Consequently it seemed essential to determine the molecular structure of this anomalous starch. Specimens of *Hericium* spp. offer unique material for such analysis because the amyloid material is stored in the hyphal walls of the fruit bodies as well as in the spores.

Portions of dried fruiting bodies of *Hericium ramosum* and *H. coralloides* were ground up and extracted in hot water for 5 minutes. The cooled, filtered extract was made to 80 percent ethanol, and the resulting precipitate was freeze-dried. The freeze-dried material was soluble in cold water and gave a purple color with iodine. Both salivary amylase and β-amylase (*5*) completely degraded the fungal polysaccharide, as evidenced by the progressive loss of iodine staining properties. Chromatography (*6*) of the β-amylase digest showed that the polysaccharide had been completely degraded to maltose. Consequently the polysaccharide extracted from *H. ramosum* and *H. coralloides* is a linear starch-type molecule containing α-1,4 glucosidic linkages only. The peak value (*7*) of the iodine spectrum was 540 nm indicating an average chain length for the amylose of about 32 glucose units in the *H. ramosum* extract. The *H. coralloides* amylose showed a peak value of 555 nm indicating an average chain length of 38 glucose units. This result contrasts with typical plant amyloses, which have chain lengths from 600 to 4000 glucose units, depending upon the source (*8*).

Not all of the freeze-dried polysaccharide of *H. ramosum* was soluble in cold water; some could only be dissolved in hot water or 1*N* NaOH. Analysis of the iodine spectra of the amylose soluble in hot water indicated an average chain length of about 45 glucose units. Thus the amylose of *H. ramosum* can be readily separated into two fractions, each having average chain lengths of 32 and 45 glucose units, respectively.

The initial treatment of the fungal tissue with hot water may have led to preferential leaching out of amylose molecules as it does from starch granules. However, overnight extraction of the tissue with 1*N* NaOH (which would completely solubilize starch granules) yielded a carbohydrate fraction identical with that from extraction with hot water. Consequently the starch of *H. ramosum* and *H. coralloides* consists of amylose only.

Since they produce only amylose, these organisms may be useful in resolving a fundamental problem of starch biosynthesis—namely, whether starch is produced by debranching of glycogen (*9*) or by initial synthesis of amylose, some of which may later be converted to branched amylopectin molecules (*10*). These organisms could also be used to study regulation of enzyme activity in vivo in that the amylose molecules produced are very short even though both starch phosphorylase (E.C. 2.4.1.1) and adenosine diphosphoglucose–glucosyltransferase (E.C. 2.4.1.b) can extensively elongate a linear molecule in vitro (*11*).

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