

NOTE

Cavities in Porous Corn Starch Provide a Large Storage Space¹JINGAN ZHAO,² MICHAEL A. MADSON,² and ROY L. WHISTLER^{2,3}

ABSTRACT

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Glucoamylase hydrolysis of corn starch granules for 4 hr at 60°C yields 14% D-glucose, producing boreholes with visible outlets on the granule surface that penetrate the granule connecting with each other in

the interior to create a cavern capable of carrying 54% or more weight of substances such as peppermint oil.

While treatment of corn starch granules with glucoamylase or α -amylase produces well-known porous starch granules (Fig. 1) (Fitt and Snyder 1984), it is now observed that the internal structure of porous granules is an open cavern (Fig. 2) that permits the granular uptake and containment of oils such as peppermint.

Such a developed structure is expected, based on earlier information on structural features of corn starch granules. Thus, it has been known that mercuric chloride solution diffuses into corn starch granules at a slow rate initially, which increases as the solution moves toward the granule center (Z. Nikuni and R. L. Whistler, *unpublished data*). This suggests a possible density gradient toward less density in the internal granule structure. A second, more likely possibility, results from simple enzyme hydrolysis. Here, the hydrolase first enters the granular microchannels (Fannon et al 1992), enlarging them into the well-known, sizable boreholes of $\approx 1 \mu\text{m}$ diameter, which approach each other and interconnect near the granular center to create a large cavity, open to the surface by way of the microchannels that became enlarged to boreholes. The resultant structure is clearly shown in Figure 2, which also shows a rippled effect within one of the boreholes, probably as a result of slight differences in density normally seen as growth rings when sections of granules are observed in the scanning electron microscope.

When the porous starch granules are immersed in peppermint oil and then immediately filtered on a fritted glass funnel and rinsed with ethanol, they retain ≈ 54 – 56% of the oil. The granules still retain 29% of the oil after standing in the open air for two months. This is in contrast to 12% of oil remaining in an open petri dish after standing in the laboratory for three days.

To determine whether the binding of peppermint oil is increased by converting the hydrophilic surface of porous starch granules to a hydrophobic surface, the porous granules were esterified with stearoyl ester groups. When these granules with hydrophobic surfaces were filled with peppermint oil, the amount of oil initially taken up was nearly the same as that for unesterified granules ($\approx 55\%$ of the total weight), with retention of $\approx 29\%$ after standing open two months in the laboratory.

MATERIAL AND METHODS

Porous Starch

Porous cornstarch was made by treating 30 g of purified corn starch with 1.8% solution of industrial-grade bacterial glucoamylase (Novo) in 120 ml of citric acid and sodium citrate buffer, pH 4.6, at 60°C. The reaction mixture was centrifuged periodically, the supernatant was decanted, and the glucose release was measured by high-performance liquid chromatography (HPLC) (CarboPac PA1, $4 \times 250 \text{ mm}$). Reaction was stopped after 14% glucose production by three resuspensions of the starch in distilled water and centrifuging with dewatering in alcohol, centrifugation, and drying in a desiccator over calcium chloride.

Microscopic Examination

Best pictures were obtained when porous starch granules were mixed with 2% agarose solution, which then was poured into a 10-cm petri dish and frozen by liquid nitrogen. After allowing the nitrogen to evaporate, the frozen mixture was quickly sliced with a safety razor blade to give a thin section. The slice was placed on an adhesive tape attached to a circular aluminum specimen stub and coated vertically with gold-palladium and photographed at an accelerator potential of 10 kV using a scanning electron microscope (JEOL JSM 840).

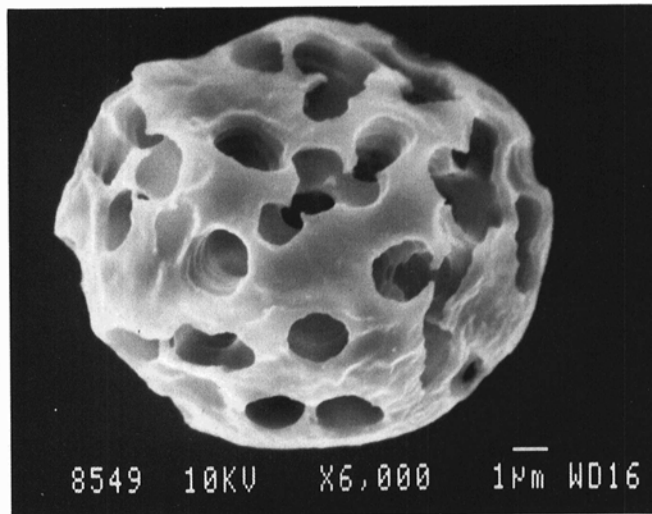


Fig. 1. Common porous corn starch granule.

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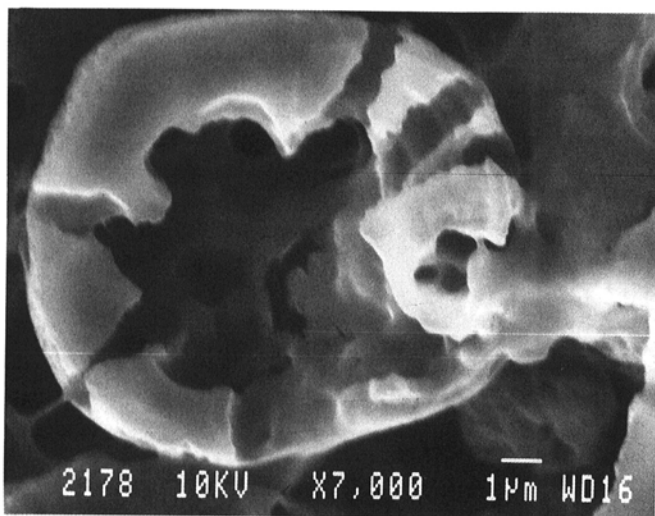


Fig. 2. Section of a porous corn starch granule viewed in a scanning electron microscope.

Stearoylated Porous Corn Starch

Vacuum-dried porous corn starch (125 g) was stirred with dry triethylamine (225 ml) for 1 hr. Anhydrous carbon tetrachloride (190 ml) was added to the uniformly stirred suspension. Then stearoyl chloride (19.0 g) in anhydrous carbon tetrachloride (95 ml) was added, dropwise, over 30 min, and the mixture was stirred for 2.25 hr. Ethanol (200 ml, 95%) was added to decompose the remaining stearoyl chloride. This mixture was stirred

1.25 hr and then centrifuged for 30 min at $1,100 \times g$. The supernatant was poured off, and the pellet was resuspended in ethanol (350 ml, 95%), and centrifuged for 15 min at $1,100 \times g$. This washing was repeated twice. The final pellet was resuspended in minimal ethanol (95%), and the granules were collected on a sintered glass funnel and vacuum-dried over CaCl_2 for 48 hr to give 123 g of stearoylated porous corn starch that remained granular. Stearoyl content was 0.85%, as determined by a modification of an analytical saponification and transesterification method described by Hauber et al (1992).

Peppermint Oil Absorption in Porous Corn Starch Granules

Peppermint oil (3 g) was slowly stirred for 1 hr with stearoylated porous corn starch or with porous corn starch (3 g). The porous corn starch granules were then separated by filtration on a sintered glass filter funnel. The peppermint oil that was not absorbed into the starch was removed by mixing the granules with 6 g of ethanol, and the mixture was filtered on a fritted glass funnel with final removal of ethanol by air-drying for one day before weighing. Thereafter, the oil-filled granules were weighed weekly.

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