A Unique Product by Spray Crystallization of Total Dextrose Hydrolysate

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ABSTRACT

A unique starch hydrolysate product of essentially α-D-glucose monohydrate in the form of small spherical beads was found to consist of discrete, flat microcrystals held together by an amorphous binding material. This unusual structure leaves a random network of void spaces. Scanning electron microscopy, X-ray diffraction, and differential thermal analysis were used to characterize the sugar and its dehydration product, anhydrous α-D-glucose. The anhydrous product exhibited an apparently modified crystalline structure with a less crystalline crust and could be reversibly hydrated back to α-D-glucose monohydrate. The rehydrated product had the same microcrystalline structure as the original product and little amorphous material, but much greater particle aggregation than either of the other two products.

A new starch hydrolysate product[3] consisting of 92% dextrose and 8% higher saccharides in small spherical bead form has been produced by controlled spray crystallization and conditioning. The unusual form of this product and its surprising bulk flow, solubility, and porosity led to a more detailed study of its

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structure. The table below summarizes some chemical and physical properties of the material (1).

Color	White
Taste	Sweet
Solubility	Water-soluble; insoluble in organic solvents
Heat of solution	−25 cal./g.
Moisture	8 to 9%
Particle size	Approximately 90% between 40 and 80 mesh
Bulk density	42 lb./ft.^{3}
pH	3.8 to 5.5
Dextrose equivalent	95 minimum
Ash	0.1% maximum
Heavy metals	5 p.p.m. maximum

It was of interest and potential utility to determine the crystalline nature of the spherical beads and the effect of dehydration and rehydration on this structure which in turn might affect some of its physical properties.

X-ray diffraction together with light and scanning electron microscopic techniques were used to elucidate structural details. Moisture and melting point (obtained by thermal analysis techniques) and optical rotation measurements were used to determine the effect of dehydration and rehydration on crystalline form.

MATERIALS AND METHODS

Sample Description

Sample A. A sample of unmodified hydrolysate was termed normal and used as the control and starting material for preparation of sample B.

Sample B. Three samples of a dehydrated product were prepared: B-1 was prepared by drying for several hours at about 140° F., B-2 was prepared by drying for 1 day at about 140° F., B-3 was prepared in the laboratory by evacuating the sample at about 85° F. and a pressure of about 25 mm. of mercury.

Sample C. Three samples of a rehydrated product were prepared from sample B-2. C-1 was prepared by rehydration using humidification at 75% r.h. C-2 was prepared by spraying with water but was thought to be incompletely rehydrated. C-3 was prepared by spraying with water until rehydration was thought to be complete.

Moisture Analysis

Moisture analyses were carried out by thermogravimetric analysis (TGA) using a duPont 950 thermogravimetric analyzer. The conditions used were as follows: approximately 20-mg. samples; heating rate, 10° C. per min.; atmosphere, air at 300 ml. per sec.; scale, 20° C. and 4 mg. per in.

DTA Melting Point

Differential thermal analysis (DTA) melting points were determined using a duPont 900 analyzer with the following conditions: sample size, 2 to 3 mm. ground and compressed in microglass tubes; reference, glass beads; heating rate,

10° C. per min.; atmosphere, nitrogen at 300 ml. per min.; T-scale, 20° C. per in.; ΔT scale, 1.0° C. per in.; and base-line slope, 0.

Optical Rotation

Specific rotation of solutions of selected samples were determined 5 min. after solution using a Model 324 polarimeter manufactured by O. C. Rudolph and Sons.

Light Microscopy

Photomicrographs were obtained by transmitted and reflected light microscopy using a Unitron and a Wild stereo microscope at magnifications of 50 to 200×.

Scanning Electron Microscopy

Scanning electron micrographs (SEMs) of sample A were obtained with a Japan Electron Optics scanning electron microscope, Type JSM. The samples were deposited with gold by sputtering and an accelerating voltage of 25 kv. was used.

SEMs of samples B-1 and C-1 were obtained from Alpha Research and Development, Blue Island, Ill. Similar conditions were used on a different instrument. However, aluminum was used in place of gold for contrast.

TABLE I. STRUCTURAL AND PHYSICAL CHARACTERISTICS OF NORMAL, DEHYDRATED, AND REHYDRATED STARCH HYDROLYSATES

Sample	Description	H_2O %	Melting Point °C.[a]	Specific Rotation degrees	Crystalline Pattern	Structural Features
A	Normal	9.2	82.5	103	A	Some particle fusion, discrete microcrystals
B-1	Dehydrated (140° F.)	1.0	...	...	B	Little particle fusion, surface crust with unusual continuous network structure for all three samples
B-2	Dehydrated (140° F.)	0.6	...	104	B	
B-3	Dehydrated (vacuum)	0.5	149	...	B	
C-1	Rehydrated (75% r.h.)	9.6	82.0	101	A	Some particle fusion, discrete microcrystals
C-2	Rehydrated (spraying)	1.8	145-147	...	A and B	Severe particle fusion
C-3	Rehydrated (spraying)	8.8	...	97	A	Some particle fusion, discrete microcrystals
α-D-glucose monohydrate		10.0	83	105 (2)	...	...
Anhydrous α-D-glucose		0	146	105	...	...
Anhydrous β-D-glucose		0	150	19.7	...	...

[a]No value obtained where blank.

X-Ray Diffraction

A General Electric laboratory X-ray diffractometer was used to obtain X-ray powder photographs of selected samples. A copper target X-ray tube was used with operating voltage and current settings of 50 kv. and 20 ma. The samples were mounted in a wedge type sample holder and exposed to radiation for 30 min.

RESULTS AND DISCUSSION

Unmodified Hydrolysate

The hydrolysate is essentially α-D-glucose monohydrate and, as shown in Table I, the normal sample (A) exhibits a moisture content of 9.2%, a melting point of 82.5° C. and a specific rotation at 5 min. of 103°. Those values compare favorably with the values given for pure α-D-glucose monohydrate, shown as 10%, 83° C., and 105° C., respectively. Figure 1 shows a light photomicrograph of the normal sample (A). Note that while individual particles average about 100 to 200 μ in diameter, many are fused into aggregates of two or more. This results in a particle size distribution having an effective mean diameter closer to 300 to 400 μ.

Figure 4 is a SEM of the normal hydrolysate (A) and clearly shows the spherical shape of the individual particles. Figure 5 shows the same sample at a much higher magnification and reveals a structure consisting of discrete, flat microcrystals bound together by an amorphous-appearing solid resulting in a network of random void spaces.

Sample A gives an X-ray pattern with intense diffraction lines indicating a high degree of crystallinity. This pattern was designated A.

Dehydrated Hydrolysate

Upon heating the hydrolysate at an elevated temperature (samples B-1 and B-2) or evacuating at low pressure and ambient temperature (sample B-3) very significant changes take place in its structure. Dehydrating to a moisture level below 1% gives a product which has a melting point of 149° C., a specific rotation of 104° at 5 min., and a X-ray diffraction pattern, designated B, different from that designated A. X-ray diffraction patterns for all samples are shown in Fig. 11.

Figure 2 shows that the individual particles of the dehydrated sample (B-2) are much less aggregated, more clearly defined as individual spheres, and not as glossy in appearance as the normal sample (A). However, Figs. 6 and 7 (sample B-1) reveal a crusty and amorphous-appearing surface with only little evidence of microcrystals. Figure 8 shows the same sample (B-1) after it was fractured to reveal the interior of a particle. The structure is clearly still crystalline in nature, but appears to be a continuous network without discrete microcrystals. This apparent difference in structure may be an artifact of fracturing the particle, but clearly the dehydrated product represents a new crystalline form.

There are only two other known crystalline modifications of glucose and they are anhydrous α-D- (m.p. 146° C.) and anhydrous β-D- (m.p. 150° C.). As shown in Table I, it is quite evident from corresponding melting point and specific rotation that the dehydrated product is anhydrous α-D-glucose.

The crystal structures of α-D-glucose (3) and β-D-glucose (4) have been determined. However, a direct comparison of powder X-ray diffraction patterns was not possible as powder patterns of the pure compounds were not readily

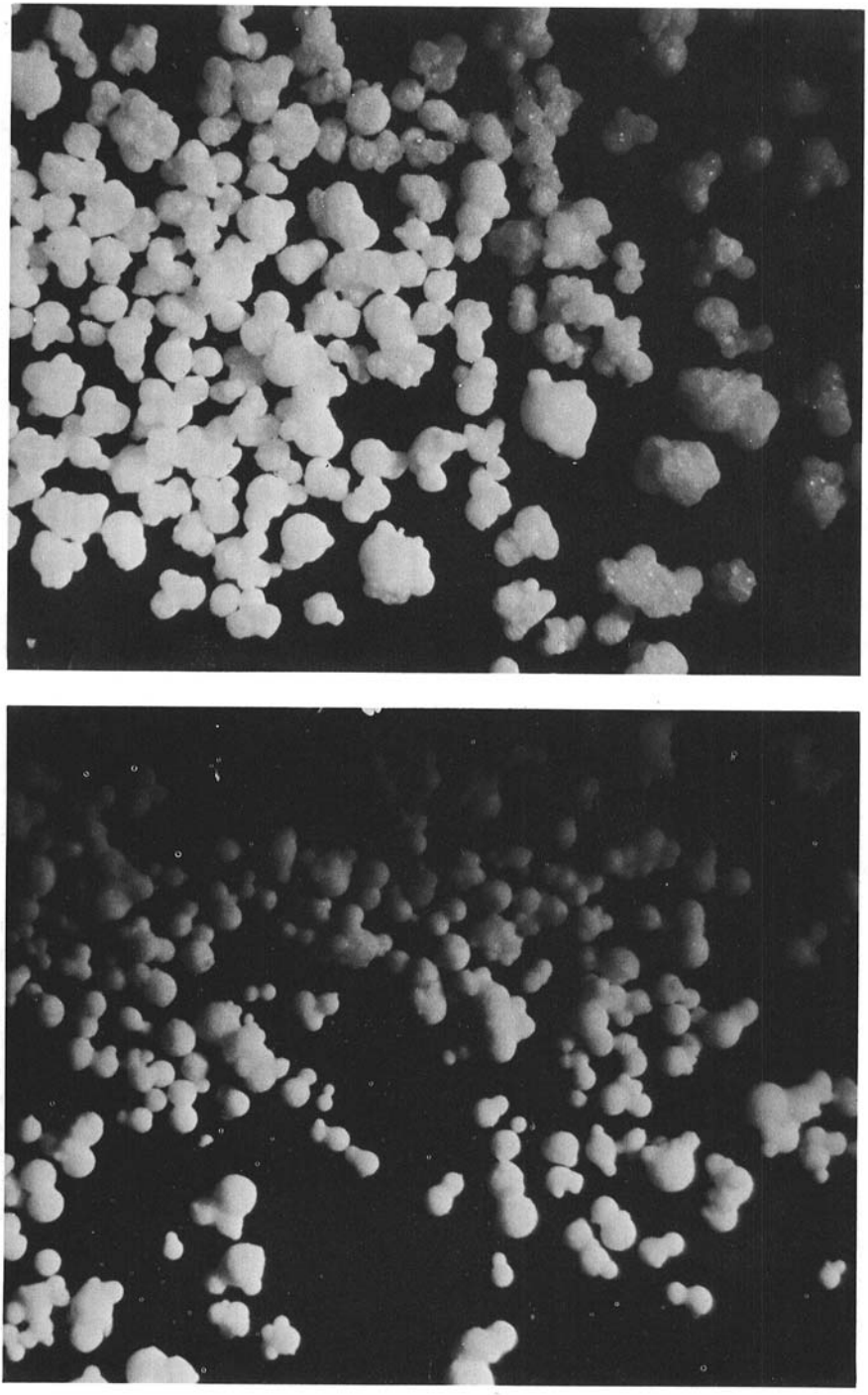
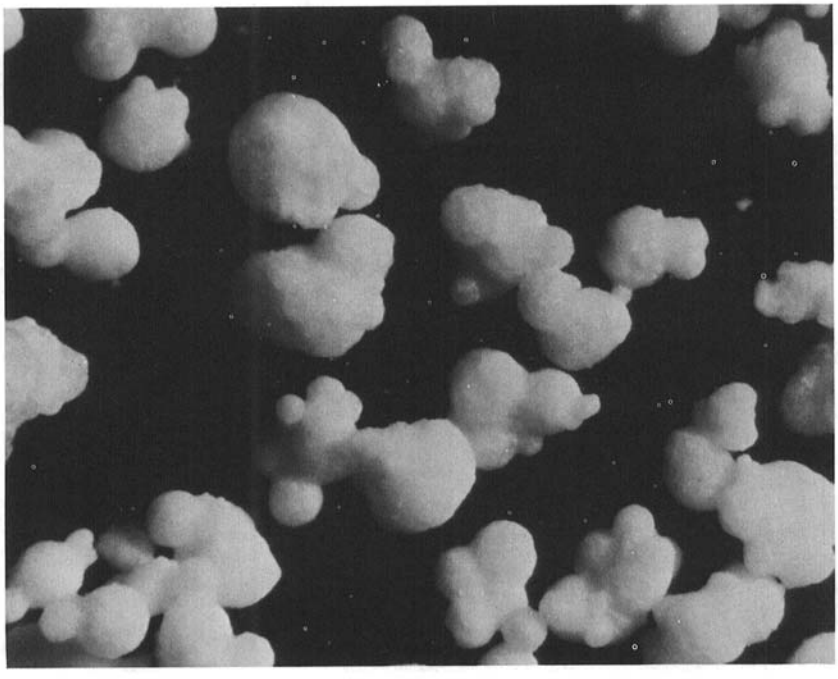


Fig. 1. (top) Normal hydrolysate (sample A); Fig. 2. (bottom) Dehydrated hydrolysate (sample B-2).



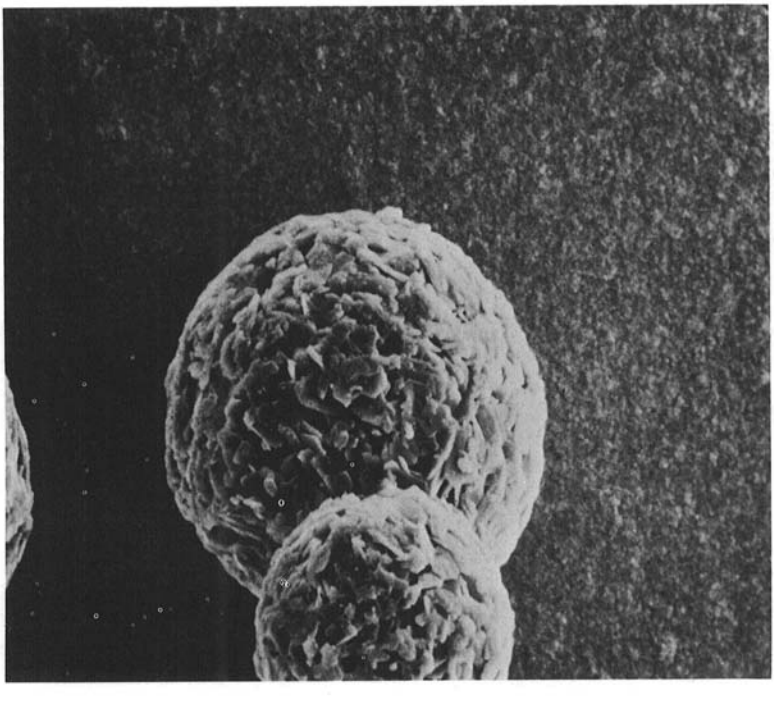
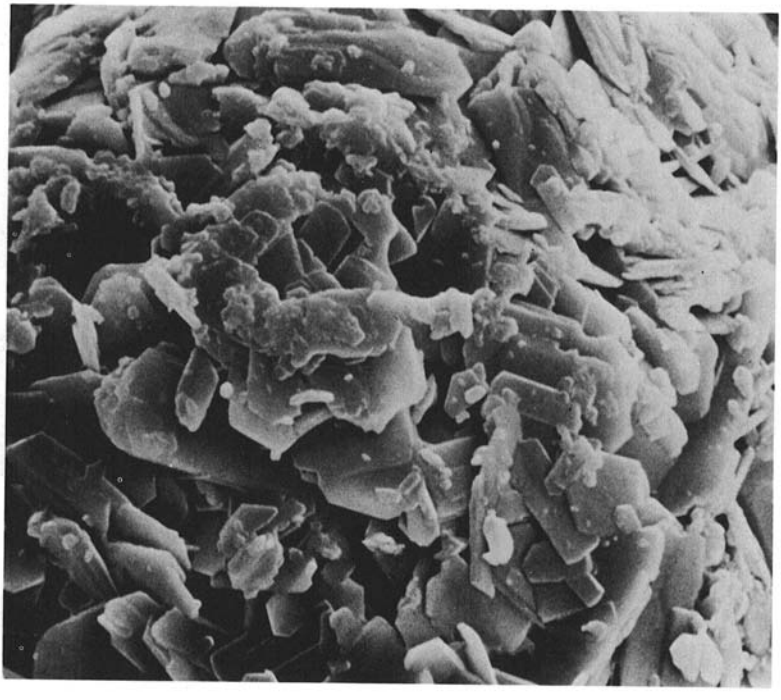


Fig. 3. (top) Rehydrated hydrolysate (sample C-2); Fig. 4. (bottom) SEM of normal hydrolysate (sample A).



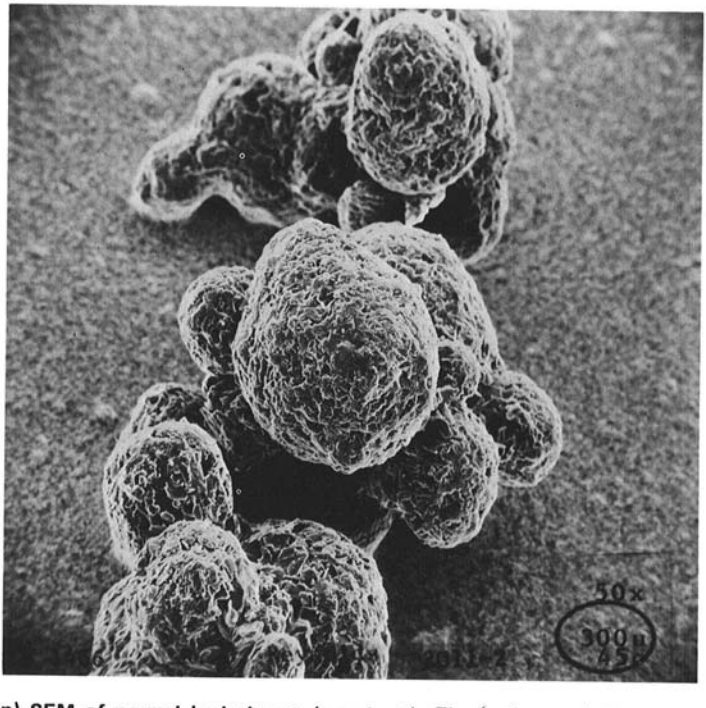


Fig. 5. (top) SEM of normal hydrolysate (sample A); Fig. 6. (bottom) SEM of dehydrated hydrolysate (sample B-1).

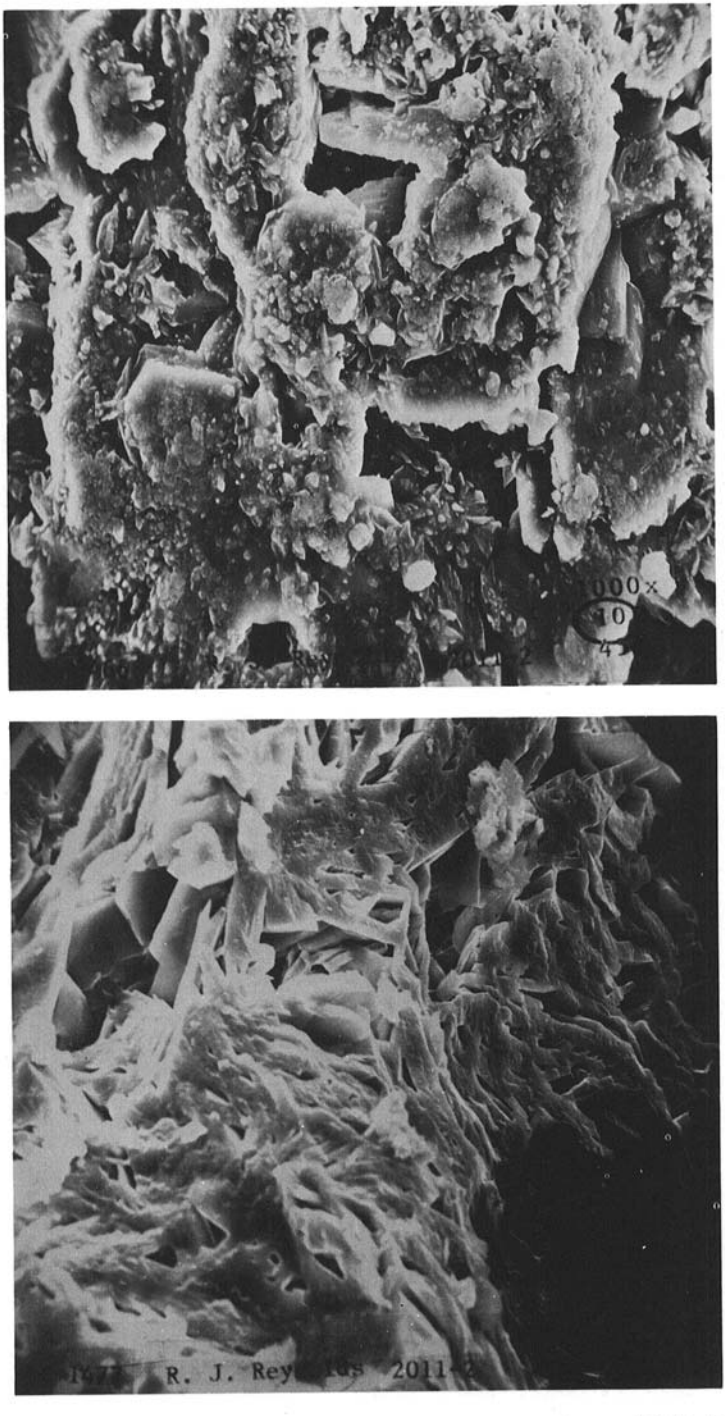


Fig. 7. (top) SEM of dehydrated hydrolysate (sample B-1); Fig. 8. (bottom) SEM of dehydrated hydrolysate (sample B-1), fractured.

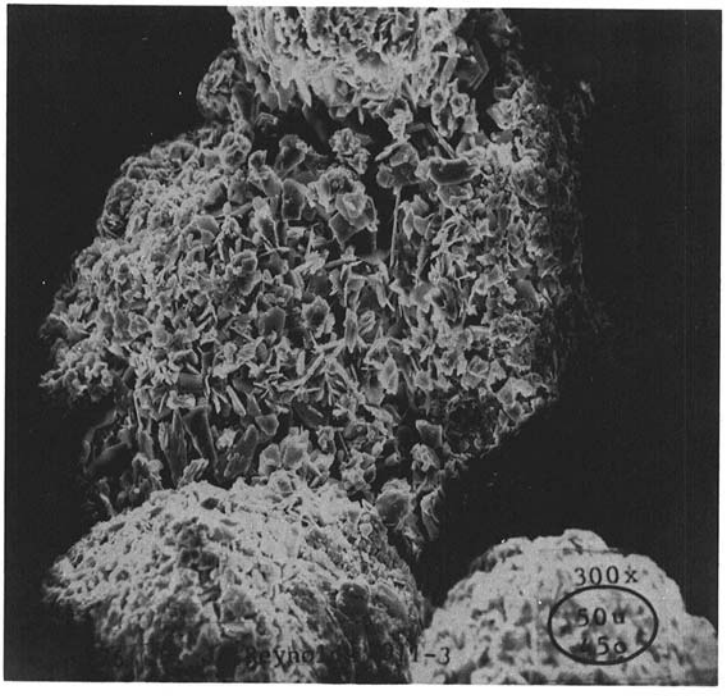


Fig. 9. (top) SEM of rehydrated hydrolysate (sample C-1); Fig. 10. (bottom) SEM of rehydrated hydrolysate (sample C-1).

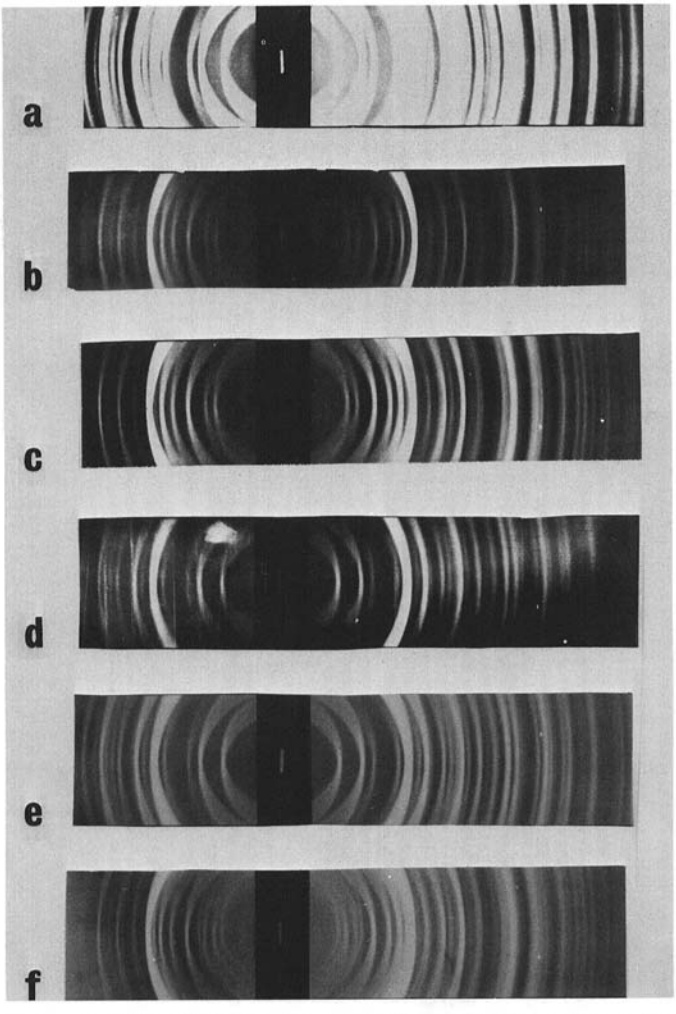


Fig. 11. X-ray powder diffraction patterns of starch hydrolysates. a, normal (sample A); b, dehydrated (sample B-1); c, dehydrated (sample B-3); d, rehydrated (sample C-1); e, rehydrated (sample C-3); f, rehydrated (sample C-2).

available. The powder pattern designated A in this work is identified as that of α-D-glucose monohydrate and the powder pattern designated B is identified as anhydrous α-D-glucose.

Rehydrated Total Sugar

Upon rehydration of the anhydrous hydrolysate it is apparent from the results shown in Table I that the normal or monohydrate is obtained again. The moisture content, melting point and specific rotation for the rehydrated product (samples C-1 and C-3) compare favorably with those for the normal product (A). Both rehydration by exposure to 75% r.h. and by spraying yield similar products.

Note that one sample (C-2) which had only 1.8% moisture was unsuccessfully rehydrated by spraying.

The rehydrated particles (Sample C-2) are much more highly aggregated than the normal sample as shown in Fig. 3. The individual particles of the rehydrated sample (C-1) have a structure almost identical to that of the normal hydrolysate (A) with perhaps even more well-defined crystallites and little or no amorphous-appearing material, as shown in Figs. 9 and 10.

The X-ray diffraction patterns (Fig. 11) of the rehydrated samples (C-1 and C-3) were identical (pattern A) with that for the normal sample (A) indicating complete reversibility from anhydrous α-D-glucose to α-D-glucose monohydrate. The sample that was incompletely rehydrated (C-2) exhibited a mixture of both patterns (A and B) confirming the fact that it was a mixture of both anhydrous and hydrated hydrolysates.

Acknowledgments

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