Short Communications

The effect of inorganic ions on the crystallization of amylodextrin

There are three modifications of the crystalline structure of starch granules[1]. The A-type have been found in cereal starches, the B-type in tuber starches and the C-type, a mixed A- and B-type, in bean and root starches, though some exceptional cases have also been found[3-6].

As is well known, starchy materials usually give B-type crystals when they are retrograded at room temperature[7], although A-type crystals have been obtained under some conditions[7-11]. Therefore, it was considered that the crystalline type of native starch granules might be controlled by the conditions of crystallization of the starchy materials in the plant. In this communication, the effect of various inorganic ions on the crystallization of amylodextrin is reported.

The amylodextrin used in this experiment was obtained from a specific kind of sweet-potato starch syrup as reported in the previous paper[11]. The degree of polymerization of the amylodextrin was 12.6. It was a linear molecule and was hydrolyzed completely by crystalline sweet-potato β-amylase to maltose and a small amount of glucose. This material could be crystallized easily as the A-, B- and C-type under different conditions, but the degree of crystallinity was higher than that in native starch granules as judged by the intensities of the diffraction lines.

To 1.1 g of the amylodextrin (1.0 g on a dry basis) in a 5-ml conical flask, 1.5 ml water was added. The amylodextrin was dissolved by immersion of the flask in gently boiling water with shaking for 1.5 min. The clear solution thus obtained was cooled for several minutes in a bath of cold water kept at the crystallization temperature. The solution was still clear. An appropriate amount (0.3–4 mmoles, as a dry powder) of a salt was added to the solution. After the salt was dissolved, the flask was tightly stoppered and different flasks were placed in incubators at a constant temperature ($7.5° \pm 0.5°$, $12° \pm 0.5°$ and $22° \pm 0.5°$) for 5 days. The precipitated amylodextrin was collected by filtration on a suction filter and treated successively with 30 ml 60 % methanol and 50 ml 80 % methanol to remove the mother liquor and the added salt. The precipitate was dehydrated with absolute alcohol and washed with ether on the suction filter. The resulting amylodextrin powder was examined by an X-ray diffractometer (Shimadzu GX-II). X-rays were Cu K_α eliminating K_β with a nickel filter. The high tension voltage was 35 kV and the current 18 mA.

As shown in curve I of Fig. 1, a B-type amylodextrin was formed when crystallized from a pure aqueous solution under the conditions described above. On the other hand, C- or A-type amylodextrin was crystallized from NaCl. The X-ray patterns approached the A-type through the C-type with increasing concentrations of the salt, as shown in curves II–V of Fig. 1. The same phenomenon was also observed to different degrees in various other salt solutions as shown in Table I. The order of effectiveness of the salts in producing A-type amylodextrin crystals was found to be $Na^+ > Li^+, NH_4^+ > K^+ > Rb^+$ for the cation series (when tested as their chlorides) and $I^- > SCN^- > Br^- > Cl^- \gg SO_4^=$ in the anion series (when tested as their potassium salts). The orders of effectiveness was similar to the lyotropic series, though the order of Na^+ and Li^+, and of I^- and SCN^- were reversed in these series[12].

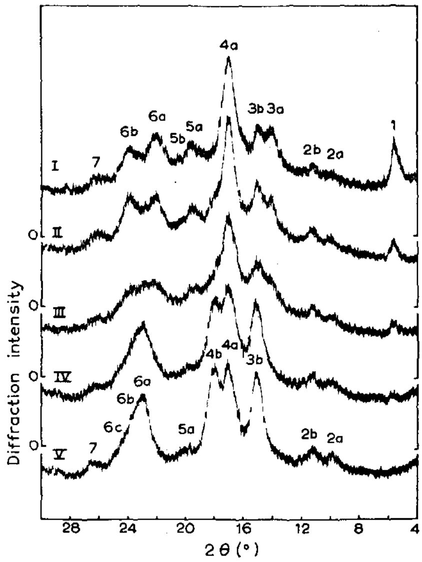

Fig. 1. X-ray-difffraction curves of amylodextrins crystallized from aq. NaCl. Concentrations (mmoles per 1.6 ml water containing 1 g amylodextrin) of NaCl were: I, none (B-type); II, 1 (C_b-type§); III, 1.5 (C_c-type§); IV, 2 (C_a-type§); V, 3 (A-type). The concentrations of amylodextrin were between 35.4 % and 38.5 % after the addition of the NaCl. This concentration change had no effect on the crystalline type, because from an aqueous solution of amylodextrin of below 46% concentration at 7.5°, the B-type crystal was always obtained.

TABLE I

CRYSTALLINE TYPES OF AMYLODEXTRIN CRYSTALLIZED FROM VARIOUS INORGANIC SALT SOLUTIONS

Crystallization temperature was 7.5°; in some cases 12°.

*Amount added salt (mmoles)**	*0*	*0.3*	*1*	*1.5*	*2*	*3*	*4*
	Crystalline type of amylodextrin						
NaCl	B		C_b	C_c	C_a	A	
NaCl (12°)	B		A				
LiCl	B		C_b		C_a	A	
NH_4Cl	B		C_b		C_a	A	
KCl	B		C_b	C_b	C_b	C_c	C_a
KCl (12°)	B	C_c	C_a				
RbCl	B				C_b	C_b	C_b
KI	B		C_c	C_a			
KCN	B		C_c	C_a			
KBr	B		C_c	C_c	C_a		
$\frac{1}{2}K_2SO_4$	B		B	B	B	B	
$\frac{1}{2}(NH_4)_2SO_4$	B		B		B	B	B

* mmoles dry salt added to the solution made by dissolving 1 g amylodextrin in 1.6 ml water.

§ C-type was divided into three sub-types; C_a: near A-type, C_c: intermediate, and C_b: near B-type.

The crystalline types of freshly precipitated amylodextrin were not only influenced by salts as described above, but by the temperature of crystallization and the concentration of the amylodextrin[13]. When the crystallization was carried out at the higher temperature and at a higher amylodextrin concentration, the A-type amylodextrin was formed even at a low salt concentration as shown in the cases of NaCl and KCl in Table I.

An exceptional result was obtained with $(NH_4)_2SO_4$, which did not have any effect on the transition from the B- to the A-type. In fact, it rather showed the reverse effect for the transition tendency, since when the salt was added to a amylodextrin solution which would produce an A-type crystal without the salt, C- and B-type crystals were produced with increasing amount of $(NH_4)_2SO_4$, and the effects of other salts were abolished (see Table II).

TABLE II

THE EFFECT OF AMMONIUM SULFATE ON THE CRYSTALLIZATION OF AMYLODEXTRIN

Conditions of crystallization	*Amount* of $(NH_4)_2SO_4$ added (mmole)*	*Crystalline type*
1 g amylodextrin dissolved in 1.6 ml water, 22°	0	A
	1	C_a
	2	C_c
	3.5	B
1 g amylodextrin and 3 mmole NaCl dissolved in 1.6 ml of water, 7.5°	0	A
	3	B

* mmoles dry salt added to a solution made by dissolving 1 g amylodextrin in 1.6 ml water.

From these results, it seems that the various salts in living plant organs might affect the crystalline types of native starch granules.

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