

TERESA FORTUNA

## AUTOHYDROLYSIS OF MONOSTARCH PHOSPHATES

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Autohydrolysis of monostarch hydrogen phosphates at boiling point of their water solutions leads to the cleavage of both the glucoside bonds of starch chain and of the ester bond of phosphoric acid.

### INTRODUCTION

The functional characteristics of potato starch depend to a great extent on the presence of phosphoric acid in its molecule [11]. In potato starch this acid is ester-bonded with the glucose radical, while in cereal starches it occurs in adsorbed form, mainly as phospholipids [7, 8]. Phosphoric acid may also be artificially introduced into starch, the result being so called starch phosphates [1, 2, 4, 5] displaying various properties depending on the amount of phosphorus added to the starch and the kind of bonds that appeared [4, 5, 13].

The chemically bonded phosphoric acid in starch gives this polysaccharide ion-exchange properties, among others [11]. It may thus be surmised that an artificial introduction of phosphoric acid radicals into the starch molecule will also lend starch phosphates cation-exchange properties. Monostarch phosphates in hydrogen form were obtained using this property [3]. The pastes of these phosphates were observed to be less viscous and more reducible than the initial phosphates. This suggests that they undergo autohydrolysis.

As is known [10], autohydrolysis of hydrogen starch is accompanied by a rapid decrease of viscosity due to fluidization of paste which ultimately becomes an almost transparent solution. Since hydrogen starch is chemically similar to monostarch phosphates, it was interesting to see whether these phosphates too undergo hydrolysis.

### MATERIAL AND METHODS

Monostarch phosphates were obtained by the Neukom method [13] as modified by Richter [13] from potato and maize starch and also from laboratory-extracted [13] native Bolero triticale starch. Industrial monostarch

phosphate was also used as substrate. Monostarch hydrogen phosphates were obtained by washing monostarch phosphate samples with 0.1 M HCl alcohol solution (according to Winkler's method for hydrogen starch [13]).

The following determinations were made in monostarch phosphates, their hydrogen forms, and in initial starches:

— total phosphorus (following mineralization of samples with concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ) and free phosphorus by Marsh's method [6]; phosphorus bonded with starch was calculated from the difference of the above contents, and the degree of phosphorus substitution was obtained;

— reductivity with dinitrosalicylic acid by Richter's method [13];

— water binding capability and solubility in water at 25 and 60°C by Richter's method [13];

— limit viscosity of starch pastes in an Ubbelohde-Rafikow viscosimeter by Richter's method [13].

Autohydrolysis of monostarch hydrogen phosphates was studied in 1% suspensions at boiling point of the solution. Samples for reductivity and free phosphorus determinations were taken 0, 0.25, 0.5, 1, 2, 3, 4 and 5 h after beginning of the process.

## RESULTS AND DISCUSSION

Table 1 lists the determined total and free phosphorus contents in monostarch phosphates (S1P) and their hydrogen forms (H-S1P) obtained from potato, maize and triticale starches and compares them with figures for the initial material (I) and for industrial phosphate and its hydrogen form. Also given in this table are figures for phosphorus bonded with starch and degree of phosphorus substitution in the obtained phosphates calculated from analytical data. As can be seen, the content of all phosphorus forms in monostarch phosphates and their hydrogen forms is several times higher than in the initial starches. The phosphorus substitution degree ranges from 0.03 to 0.04, the exception being the industrial monostarch phosphate and its hydrogen form for which this figure was 0.08 and 0.05 respectively. This difference results from the fact that the technology used in industry [12] produces a starch phosphate with a higher substitution degree. However, this kind of phosphate contains large amounts of free phosphorus which is eliminated during the obtaining of the hydrogen form.

Table 2 contains results of reducibility, water binding capacity and water solubility at 25 and 60°C, and also of limit viscosity of monostarch hydrogen phosphates, compared with figures for initial material and monostarch phosphates. The figures show a clear increase of reducibility in monostarch hydrogen phosphates which may be attributed to the autohydrolytic effect of hydrogen ions on the molecule of this polysaccharide. A similar phenomenon was observed in hydrogen starch [10]. An increase reducibility was also apparent in the initial triticale starch, something observed also in earlier studies [2].

Table 1 Phosphorus content and degree of phosphorus substitution in monostarch hydrogen phosphates (H-SIP) compared with figures for initial starch (I) and monostarch phosphates (SIP)

Determinations	Potato starch			Maize starch			Triticale starch			Industrial phosphate	
	I	SIP	H-SIP	I	SIP	H-SIP	I	SIP	H-SIP	SIP	H-SIP
Total phosphorus (mg P/100 g d.m.)	78.2	935.2	724.6	19.6	839.5	697.9	41.4	527.9	517.1	2078.3	1056
Free phosphorus (mg P/100 g d.m.)	1.2	137.6	16.7	0.8	61.7	27.9	0.6	45.7	12.8	575.7	36.7
Bounded phosphorus (mg P/100 g d.m.)	77.0	797.6	709.9	18.0	777.8	670.0	40.8	482.2	504.3	1502.6	1019.3
Phosphorus substitution degree	0.00	0.04	0.04	0.00	0.04	0.04	0.00	0.03	0.03	0.08	0.05

Table 2. Reducibility, water binding capacity, water solubility and limit viscosity of monostarch hydrogen phosphates (H-SIP) compared with figures for initial material (I) and monostarch phosphates (SIP)

Determinations	Potato starch			Maize starch			Triticale starch			Industrial phosphate	
	I	SIP	H-SIP	I	SIP	H-SIP	I	SIP	H-SIP	SIP	H-SIP
Reducibility (% glucose)	0.44	0.72	2.81	1.07	0.86	3.21	1.85	1.17	3.25	0.70	1.80
Water binding capacity (g/1 g d.m.)											
at 25°C	2.14	7.3	3.5	2.2	13.2	3.1	2.2	9.0	3.3	55.9	45.4
at 60°C	14.2	86.9	74.7	3.0	53.8	31.3	8.1	50.9	39.8	94.1	68.3
Solubility in water (%)											
at 25°C	0.1	20.4	19.1	0.2	23.8	16.3	0.9	17.5	17.1	29.3	51.6
at 60°C	7.7	69.9	85.4	1.1	65.7	82.5	4.9	61.2	84.2	50.6	98.9
Limit viscosity (100 cm <sup>3</sup> /g)	2.46	0.83	0.15	1.82	0.81	0.13	1.87	0.74	0.16	0.96	0.23

Table 3. Autohydrolysis of monostarch hydrogen phosphates

Hydrolysis duration (h)	Hydrolysate reducibility (% glucose)				Free phosphorus content (mg P/100 g d.m.)			
	1	2	3	4	1	2	3	4
0	3.78	2.50	5.25	2.22	20.3	28.8	17.5	23.3
0.25	6.14	3.25	5.50	4.11	38.4	39.7	25.0	55.1
0.50	5.87	7.25	7.25	5.69	56.0	55.7	35.3	77.8
1.0	8.36	9.0	9.0	7.52	97.1	84.0	58.2	147.0
2.0	14.03	12.75	10.75	10.38	163.0	156.1	113.2	226.3
3.0	14.87	13.5	13.5	16.35	226.8	217.2	153.1	348.7
4.0	17.54	17.25	15.5	21.93	274.3	271.5	183.7	463.1
5.0	20.1	18.25	16.0	29.76	349.6	302.1	217.1	562.5

- 1 — potato monostarch hydrogen phosphate
- 2 — maize monostarch hydrogen phosphate
- 3 — triticale monostarch hydrogen phosphate
- 4 — industrial monostarch hydrogen phosphate

Figures for water binding and water solubility were higher in monostarch phosphates and their hydrogen forms, at both the studied temperatures, than in the initial starches. Already at 25°C the monostarch phosphates, especially the industrial one, exhibit a high water binding capacity and high water solubility. After transformation into the hydrogen form, figures for water binding at this temperature drop sharply in all phosphates except for the industrial hydrogen monostarch in which this decrease is slight. At 60°C too the monostarch phosphates exhibit the highest water binding capacity, and this situation is in agreement with earlier studies [2, 3] and literature reports [13, 14] confirming the substantial increase of water binding capacity in starch phosphates.

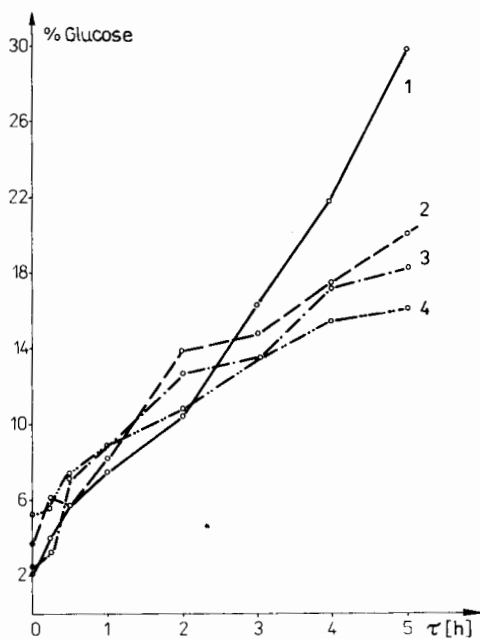


Fig. 1. Reducibility of monostarch hydrogen phosphates during autohydrolysis; 1 — industrial monostarch hydrogen phosphate, 2 — potato monostarch hydrogen phosphate, 3 — maize monostarch hydrogen phosphate, 4 — triticale monostarch hydrogen phosphate

The solubility of the studied starch phosphate preparations at 25°C and also at 60°C is much greater than of initial starches. At the higher temperature the hydrogen forms of monostarch phosphates display the greatest solubility in water, this being the result of autohydrolysis occurring in the conditions of analysis and leading to depolymerization of particles and their increased solubility.

The monostarch hydrogen phosphates are, generally speaking, characterized by very low limit viscosity, well below unity, namely from 0.13 to 0.23 (100 cm<sup>3</sup>/g); in initial starches this viscosity is between 1.82 to 2.46 (100 cm<sup>3</sup>/g).

The hydrogen forms of all monostarch phosphates are thus highly reducible, more soluble in water at 60°C, and marked by low limit solubility, all this suggesting that they undergo autohydrolysis during analyses.

This hypothesis was checked by analyzing 1% water suspensions of the studied hydrogen forms of monostarch phosphates in the course of 5-h heating at boiling point of the solution. The results are collected in Table 3, and they show that as hydrolysis progresses not only reducibility increases considerably, but so does free phosphorus content. This is evidence of glycoside bonds hydrolysis and of phosphate deesterification. The changes of reducibility are represented graphically in Fig. 1 while changes in free phosphorus content over hydrolysis time — in Fig. 2. A directly proportional dependence of phosphorus substitution degree on autohydrolysis rate of monostarch hydrogen phosphates is clearly evident.

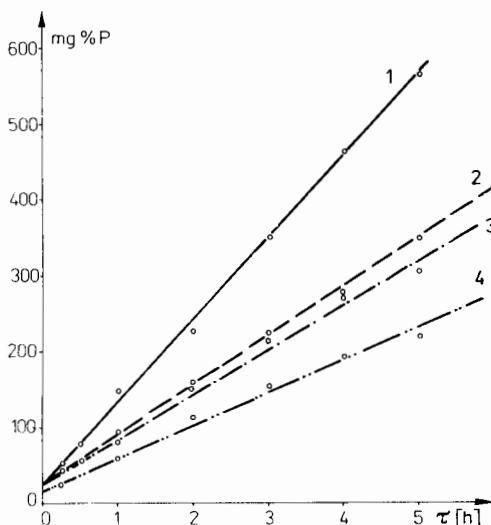


Fig. 2. Free phosphorus content during autohydrolysis of monostarch hydrogen phosphates; see Fig. 1 for explanations

## CONCLUSIONS

1. Hydrogen forms of monostarch phosphates obtained from potato, maize and triticale and also of industrial monostarch phosphates undergo autohydrolysis leading to increased reducibility of hydrolyzates and liberation of o-phosphoric acid.

2. The rate of monostarch hydrogen phosphates autohydrolysis is directly proportional to their phosphorus substitution degree.

3. The obtained monostarch hydrogen phosphates differ from monostarch phosphates by:

- a lower water binding capacity and solubility in water, particularly at 60°C,
- higher reducibility, and
- lower limit viscosity.

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#### AUTOHYDROLIZA FOSFORANÓW JEDNOSKROBIOWYCH

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#### Streszczenie

Z krochmalu ziemniaczanego, kukurydzianego oraz skrobi pszenicy otrzymano w skali laboratoryjnej fosforany jednoskrobiowe metodą Neukoma. Z fosforanów tych oraz przemysłowego fosforanu jednoskrobiowego sporządzono formy wodorowe przez przemywanie próbek roztworem kwasu solnego. W otrzymanych preparatach oznaczono: zawartość fosforu całkowitego i fosforu wolnego, zdolność wiązania wody i rozpuszczalność w wodzie w temp. 25 i 60°C, zdolność redukcyjną i lepkość graniczną za pomocą wiskozymetru Ubbelohde-Rafikov. Przebadano autohydrolizę 1% wodnych suspensji form wodorowych fosforanów jednoskrobiowych w temperaturze wrzenia roztworu w ciągu 5 h. W trakcie autohydrolizy pobierano próby, które badano na redukcyjność i zawartość fosforu wolnego.

Zaobserwowano, że w miarę przebiegu autohydrolizy znacznie wzrasta redukcyjność i zawartość fosforu wolnego, co świadczy o hydrolizie wiązań glikozydowych w łańcuchu skrobiowym oraz hydrolizie estrowego wiązania kwasu fosforowego. Szybkość autohydrolizy form wodorowych fosforanów jednoskrobiowych zależy od ich stopnia podstawienia fosforem. Ponadto zaobserwowano, że formy wodorowe fosforanów jednoskrobiowych odznaczały się wyższą redukcyjnością, mniejszą zdolnością wiązania wody i większą rozpuszczalnością w wodzie, zwłaszcza w temp. 60°C oraz niższą lepkością graniczną w stosunku do fosforanów jednoskrobiowych.