

TERESA FORTUNA

PHYSICO-CHEMICAL PROPERTIES OF MONOSTARCH HYDROGEN PHOSPHATES OF VARIOUS ORIGIN*)

Department of Carbohydrates Technology, Agricultural University, Cracov

Key words: monostarch hydrogen phosphates, physico-chemical characteristics of monostarch hydrogen phosphates, potato, wheat, triticale starch.

Monostarch phosphates were obtained from potato, wheat and triticale starch. They were converted into monostarch hydrogen phosphates whose, physico-chemical properties were studied.

The decrease of viscosity and increase of reducibility of the hydrogen forms of starch phosphates are accounted for by autohydrolysis, the course of which depends on the origin of starch.

INTRODUCTION

In the reaction of starch with estrifying agents, it is possible to introduce both to amylose and amylopectin, acid groups connected by ester bonds with units of anhydrous glucose, forming the so-called starch esters [1, 4, 6]. By introduction of residues of phosphoric acid to starch molecules, it is possible to obtain the so-called starch phosphates [4, 5, 6, 10]. Depending on the amount of phosphate introduced and type of created bonds, these phosphates are characterized by various functional properties [1, 4]. Potato starch is such a natural starch phosphate.

The presence of chemically bound phosphoric acid to this starch, determines its numerous physico-chemical properties including ion-exchange [9]. It can be expected that an artificial introduction of o-phosphoric acid residues into starch molecules during the process of obtaining starch phosphates should impart to them also ion-exchange properties.

During the studies on the properties of starch phosphates of various origin [3], it was decided to make use of these properties with a view to obtaining hydrogen starch phosphates hoping to obtain preparations with interesting physico-chemical properties. For this purpose, monostarch phosphates were

*) The study was subsidized by the Committee of Food Technology and Chemistry of the Polish Academy of Sciences.

produced from potato, wheat and triticale starch and then, they were converted into hydrogen form and the major properties of the obtained products were examined.

MATERIAL AND METHODS

For these studies, potato starch produced in the Potato Industry Works at Piła, wheat starch manufactured in the Federal Republic of Germany and triticale starch obtained by a laboratory method [11] from the „Lasko” variety, were used.

The process of obtaining monostarch phosphate (MP) was conducted by the method of Neukon [7], modified by Richter [11], consisting in a calcination of starch with Na_2HPO_4 and NaH_2PO_4 at 160°C for 4 hours. The hydrogen form of monostarch phosphate (MHP) was obtained by washing a 30-g sample of monostarch phosphate with 0.05 M alcohol solution of HCl ($5 \times 150 \text{ cm}^3$ of 0.0 M HCl for 15 min and then washing it out with alcohol).

In the obtained monostarch phosphates, in their hydrogen forms, and in the initial starches, the following determinations were made:

— the content of total phosphorus (after previous mineralization of the sample with concentrated H_2SO_4 and HNO_3) and of free phosphorus by the method of Marsh [8]. The content of bound phosphorus was calculated from the difference,

— the corrected water-binding capacity and solubility in water at 60°C (11),

— characteristics of 7.2% water dispersions of starch in a rotary viscosimeter Rheotest 2, based on the modified method of Winkler [2, 13]. The measurements were done at the following points of pasting characteristics:

temperature of pasting (t_k),

maximum viscosity (η_{max}),

temperature at maximum viscosity (t_{max}),

viscosity at 96°C ($\eta_{96^\circ\text{C}}$),

viscosity after 20 minutes of heating at 96°C ($\eta_{96^\circ\text{C}/20'}$),

viscosity after cooling down at 50°C ($\eta_{50^\circ\text{C}}$),

viscosity at the rate of $8 \text{ a} = 27 \text{ r.p.m.}$

— reducing capacity with dinitrosalicylic acid by the method of Richter (11).

RESULTS AND DISCUSSION

Table 1 shows the results of analyses of the content of total and free phosphorus in monostarch phosphates (MP) and their hydrogen forms (MHP) obtained from potato, wheat and triticale starches, in comparison with the initial material. The Table indicates also the level of phosphorus bound to starch, calculated from these analytical data and on this basis, the degree of substitution

Table 1. Content of phosphorus in monostarch phosphates in hydrogen form (MHP) in comparison with the initial starch (S) and monostarch phosphate (MP)

Type of determination	Potato starch			Wheat starch			Triticale „Lasko“ starch		
	S	MP	MHP	S	MP	MHP	S	MP	MHP
Total phosphorus (mg P/100 g ss)	81.9	744.1	538.2	62.0	589.9	533.3	44.6	528.5	524.1
Free phosphorus (mg P/100 g ss)	1.6	199.1	9.7	0	55.6	16.6	1.3	16.3	15.7
Bound phosphorus (mg P/100 g ss)	80.3	545.0	528.5	62.0	534.3	516.7	43.3	512.2	508.4
Degree of substitution with phosphorus	0.00	0.03	0.03	0.00	0.03	0.03	0.00	0.03	0.03

of the obtained phosphates by phosphorus, was calculated^{*)}. The Table shows that the level of phosphorus bound to monostarch phosphates and to their hydrogen forms is several times higher than in initial starches and the calculated degree of substitution with phosphorus in all phosphates is equal and amounts to 0.03. The low degree of substitution with phosphorus is evidence that these preparations may be used in food production.

The relatively high content of free phosphorus in monostarch phosphates compared with the initial starch, is caused by the methodical factors. During the process of obtaining monostarch phosphate, phosphates used for estrification, under the condition of the applied methodology are not completely removed. The removal of free phosphorus takes place to a large extent during the process of obtaining the hydrogen form (intensive washing of monostarch phosphate with acid and with ethyl alcohol); in cereal starches this process is much slower.

Table 2 lists the results of water-binding capacity and solubility in water at 60° and the reducibility of the examined preparations in comparison with the initial starches. The data contained in the Table show that water-binding capacity and solubility in water are increased considerably after estrification of starch with o-phosphoric acid and are maintained at the same level also after converting monostarch phosphate into hydrogen form (MHP)**. In case of hydrogen monostarch phosphate obtained from potato starch, the water-binding capacity is almost 3 times higher than for the initial starch whereas solubility is as many as 7 times higher. Monostarch phosphates obtained both from wheat starch and triticale starch as well as their hydrogen forms are characterized by a

*) $\frac{\text{mole of P bound to starch}}{\text{mole of glucose residue}}$

***) The hydrogen form of monostarch phosphate shows even a rising tendency.

Table 2. Water-binding capacity, solubility in water and reducibility of monostarch phosphates in hydrogen form (MHO) in comparison with the initial starch (S) and monostarch phosphates (MP)

Type of determination	Potato starch			Wheat starch			Triticale starch		
	S	MP	MHP	S	MP	MHP	S	MP	MHP
Water-binding capacity at 60°C (g/l g ss)	15.5	39.3	44.1	5.2	47.1	51.6	6.1	56.0	68.3
Solubility in water at 60°C, %	7.3	49.1	52.8	2.3	49.1	52.8	4.8	59.2	64.8
Reducibility of glucose %	0.43	0.89	1.88	0.70	1.10	1.84	1.74	1.33	1.97

water-binding capacity and solubility in water several times higher than the initial starches. These observations are consistent with literature data [4, 12] confirming a considerable increase of water-binding capacity in modified starches.

As regards the reducibility of initial starches, a higher reducibility of triticale starch than of wheat starch, and especially of potato starch, has been observed. Probably, the reason for this phenomenon is a higher enzymatic activity in triticale grain which may cause the partial degradation of starch as early as in the stage of grain [14]. Monostarch phosphate from triticale starch is the only one to reveal a lower reducibility than initial starch before modification. This may be due to the fact that in the process of obtaining phosphates (calcination at 160°C) depolymerization of starch molecules takes place and part of the soluble products of dextrinization is washed out in final stage of obtaining the products. On the other hand, a distinct increase of reducibility is noticed in hydrogen forms of monostarch phosphates (MHP). It may be explained by the autohydrolytic action of hydrogen ions (present in a hydrogen form of starch phosphate) on the molecule of this polysaccharide.

Table 3 presents the results of pasting characteristics of water dispersion of starch with a concentration of 7.2%, determined in a rotary viscosimeter Rheotest 2. It results from this Table that all monostarch phosphates in a hydrogen form reveal a very low viscosity (below the sensitivity of the instrument used for the measurement*). This is caused by the autohydrolysis of starch occurring during heating of pastes in a Rheotest 2 viscosimeter.

The data referring to the characteristics of pasting of monostarch phosphates confirm earlier observations [3], being evidence of a lower temperature of pasting and temperature at a maximum of viscosity, and of lower values of viscosity in comparison with the initial starch (except for the maximum of viscosity in

*) Especially the hydrogen forms of monostarch phosphates obtained from potato and wheat starches.

Table 3. Characteristics of pasting of 7.2% water pastes of monostarch in hydrogen form (MHP), in comparison with the initial starch (S) and monostarch phosphate (MP)

Type of starch		Parameters of pasting characteristics					
		tk (°)	max (mPa·s)	t max (°C)	96°C (mPa·s)	96°C/20' (mPa·s)	50°C (mPa·s)
Potato starch	S	64.5	4788	77	30	323	3272
	MP	57	184	68	96	54	138
	MHP*	—	x	—	x	x	x
Wheat starch	S	88	182	96	182	197	299
	MP	45.5	508	60	96	18	150
	MHP*	—	x	—	x	x	x
Triticale starch	S	87	173	93	152	146	289
	MP	40.5	514	53	18	6	60
	MHP*	54.5	36	55	x	x	12

* Results at the limit of sensitivity of the measuring instrument

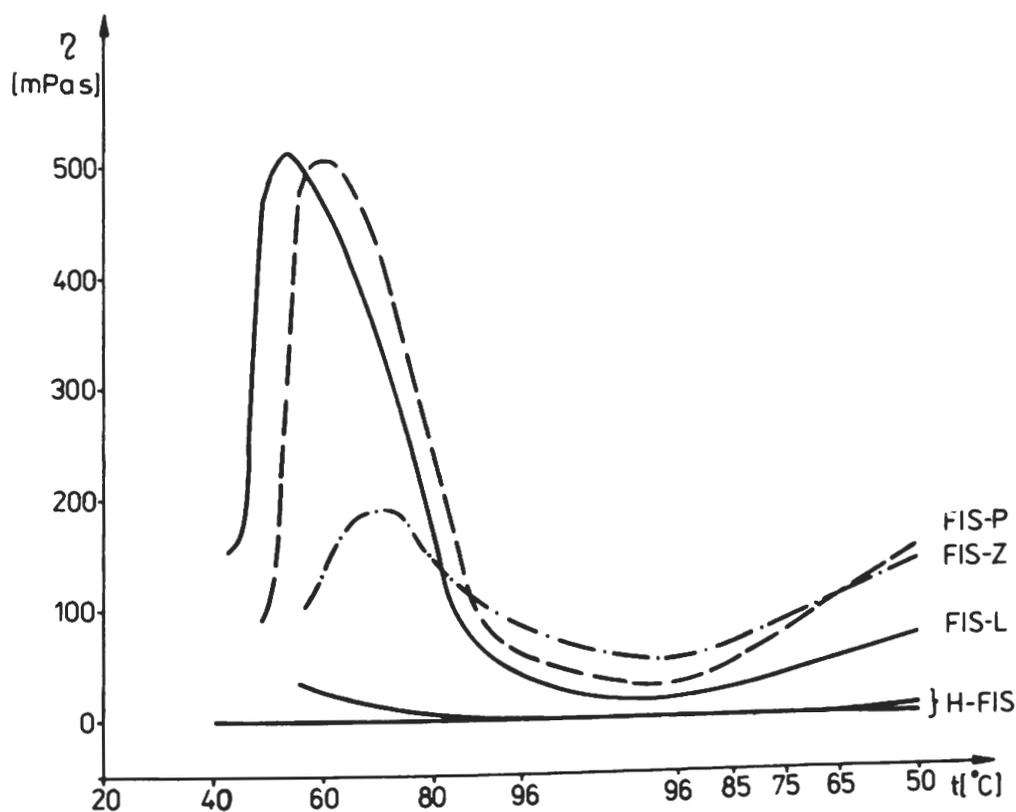


Fig. 1 Characteristics of pasting of 7.2% water dispersions of monostarch phosphates and their hydrogen forms performed in a rotary viscosimeter Rheotest 2; MPP—potato monostarch phosphate, MPW—wheat monostarch phosphate, MPT—triticale „Lasko” monostarch phosphate, MHP—hydrogen form of monostarch phosphates

phosphates obtained from cereal starches and viscosity at 96°C for phosphate obtained from potato starch). An interesting phenomenon in this case is a higher maximum viscosity of monostarch phosphates obtained from cereal starches than of phosphate obtained from potato starch. This viscosity is also higher than in the initial cereal starches. In order to illustrate better the results obtained, the pasting characteristics have been graphically presented in Fig.

The conducted studies show that physico-chemical properties of hydrogen monostarch phosphates are influenced by the properties of the initial starch, i.e. by the origin of starch. In comparison with monostarch phosphates, their hydrogen forms reveal autohydrolytic properties which are expressed in an increased reducibility and decrease in viscosity of their pastes.

CONCLUSIONS

1. The properties of hydrogen monostarch phosphates depend to a small degree only on their origin, that is on the properties of the initial starch. The greatest differences have been observed in water-binding capacity.

2. The tested hydrogen forms of monostarch phosphates, in comparison with the initial phosphates were characterized by a higher water-binding capacity and solubility in water at 60°C.

3. The obtained hydrogen forms of phosphates, compared to monostarch phosphates, demonstrated a very low viscosity in all measured parameters of pasting characteristics.

4. The decrease of viscosity and increase of reducibility of the hydrogen forms of monostarch phosphates are evidence of their autohydrolysing capacity.

LITERATURE

1. Boruch M., Nowakowska K.: *Zeszyty Naukowe Politechniki Łódzkiej* 1983, **37**, 39.
2. Fortuna T., Gambuś H., Nowotna A., Pałasiński M.: *Acta Alimentaria Polonica* 1985, **11**, 53.
3. Fortuna T.: *Zeszyty Naukowe Akademii Rolniczej w Krakowie* (in press).
4. Grześkowiak M.: *Wydawnictwo Naukowe Uniwersytetu im. A. Mickiewicza w Poznaniu* 1978, **28**, 77.
5. Heyns K., Mahlmann H.: *Deutsche-Lebensmittel-Rundschau* 1981, **77**, 121.
6. Koch H., Bommer H. D., Koppers J.: *Starch/Stärke* 1982, **34**, 16.
7. Neukom H.: *US Patent* 2 884 412, 1959.
8. March B. B.: *Biochem. Biophys. Acta* 1959, **32**, 357.
9. Pałasiński M.: *Starch/Stärke* 1980, **32**, 405.
10. Remiszewski M.: *Przem. Spoż.*, 1986, **40**, 110.
11. Richter M., Augustat S., Schierbaum, F.: *Ausgewählte Methoden der Stärkchemie*. VEB Fachbuchverlag, Leipzig 1968, 53.
12. Świdorski F.: *Acta Alimentaria Polonica* 1977, **27**, 115.
13. Winkler S., Luckov L., Donie H.: *Starch/Stärke* 1971, **23**, 235.
14. Wolski T.: *Nowe Rolnictwo* 1973, **22**, 8.

Manuscript received: March, 1988

Author address: 30-059 Kraków Mickiewicza 24/28

T. Fortuna

FIZYKOCHEMICZNE WŁAŚCIWOŚCI FOSFORANÓW JEDNOSKROBIOWYCH W FORMIE WODOROWEJ RÓŻNEGO POCHODZENIA

Zakład Technologii Węglowodanów, AR, Kraków

Streszczenie

Uzyskano z krochmalu ziemniaczanego, pszennego oraz skrobi pszenżytniej fosforany jedno-skrobiowe o stopniu podstawienia 0,03. Z fosforanów tych otrzymano formę wodorową przez przemywanie próbek roztworem kwasu solnego. W otrzymanych fosforanach, ich formach wodorowych oraz skrobiowych wyjściowych oznaczono: zawartość fosforu całkowitego i fosforu wolnego, zdolność wiązania wody i rozpuszczalność w wodzie w temp. 60°C, zdolność redukcyjną oraz charakterystykę kleikowania w wiskozymetrze rotacyjnym Rheotest 2. Formy wodorowe fosforanów skrobiowych odznaczały się wyższą zdolnością wiązania wody i rozpuszczalnością w wodzie w temp. 60°C niż wyjściowe fosforany skrobiowe. Ponadto ich formy wodorowe wykazywały bardzo niską lepkość we wszystkich punktach pomiaru charakterystyki kleikowania (tab. 3) w stosunku do wyjściowych fosforanów skrobiowych. Zaobserwowano również wzrost redukcyjności (tab. 2) w przypadku form wodorowych fosforanów skrobiowych. Zarówno spadek lepkości kleików, jak również podwyższona redukcyjność form wodorowych fosforanów skrobiowych, wynikają z ich zdolności do autohydrolizy.