

# Effects of Low Molecular Weight Carbohydrates on Farinograph Characteristics and Staling Endotherms of Wheat Flour-Water Doughs

L. Duedahl-Olesen,<sup>1,2</sup> W. Zimmermann,<sup>1</sup> and J. A. Delcour<sup>3</sup>

## ABSTRACT

Cereal Chem. 76(2):227–230

Glucose, maltose, maltotriose, maltotetraose,  $\alpha$ - and  $\gamma$ -cyclodextrins, and maltodextrins from potato starch (average degree of polymerization [DP] of 17) and maize starch (average DP of 20) were added to wheat flour-water doughs at levels of 1.0 and 3.0% (based on dry flour weight). Additions of 3.0% (w/w)  $\alpha$ - and  $\gamma$ -cyclodextrins increased the 500 farinograph unit (FU) consistency by 174 and 193 FU, respectively, while the same levels of potato and maize starch dextrins increased the consistency by 32 and 21 FU, respectively. Expressed in an alternative way, the water

absorption corresponding to 500 FU consistency was increased by 4.2 and 4.6% after addition of 3.0% (w/w)  $\alpha$ - and  $\gamma$ -cyclodextrins, respectively. Differential scanning calorimetry was used to evaluate the direct effects of addition of low molecular weight carbohydrates on amylopectin recrystallization in baked flour-water doughs. A significant reduction in amylopectin recrystallization was found after the addition of 3.0% (w/w)  $\gamma$ -cyclodextrin after seven days of storage of the baked wheat flour-water dough.

Maltooligosaccharides are starch hydrolysis products. These compounds are either linear or branched and can prevent retrogradation of starch-containing foods and crystallization of sucrose (e.g., in frozen food). They reduce color formation and impart a more uniform distribution of moisture in foods over a wide range of relative humidities (Schenck and Hebeda 1992). Staling (firming) of bread involves amylopectin as the major starch component, since the retrogradation of amylose is completed well before the firming associated with staling of bread is detected (Schoch and French 1947). Addition of  $\alpha$ -amylase to bread decreases staling of the bread. Lin and Lineback (1990) found that added  $\alpha$ -amylase, when acting on amylopectin, partially degraded it to branched-chain dextrins of low molecular weight. The antistaling effect of the branched-chain products is believed to be caused by a decrease of or an interference with the crystallization (retrogradation) of amylopectin or from interference with the formation of other interactions. Martin and Hosney (1991) found that firming was retarded in bread supplemented with an  $\alpha$ -amylase producing linear malto-oligosaccharides with a degree of polymerization (DP) of 3–9. High molecular weight dextrins did not have an antifirming effect on the bread crumb. Every et al (1992) analyzed the relationship between crumb firmness and the levels of three dextrin classes in the bread crumb water extract. High levels of maltooligosaccharides of DP 3–10 extracted from the bread crumb were related to less bread crumb firmness. Addition of maize maltooligosaccharides of DP 3–10 at a level of 1.8% (based on flour dry weight) left the crumb firming rate unaffected. Additions of 3.6% dextrins of the size classes DP 2–200+ and DP 11–200+ slightly increased the firming. Levels higher than 3.6% (based on flour dry weight) resulted in lower bread volume and a doughy and sticky crumb (Every et al 1992).

$\alpha$ -Amylase antistaling effects in bread may be due to changes in the structure of starch. These structural changes might be directly involved in the antistaling mechanism, or the low molecular weight compounds formed by the cleavage of the starch might cause an antistaling effect. Addition of  $\alpha$ -amylase to doughs contributes to both mechanisms. In the case of the addition of carbohydrates, the only effect obtained is the entanglement of the added dextrins with starch or other components in the dough. We here describe the

production of maltotetraose (DP 4) and the effect of a variety of maltooligosaccharides on the retrogradation of starch in a baked flour-water dough to obtain a better understanding of the role of  $\alpha$ -amylase on bread staling.

## MATERIALS AND METHODS

### Carbohydrates

The carbohydrates used were D-glucose, maltose (Sigma, St. Louis, MO); maltotriose (Fluka, Chemie AG, Buchs, Switzerland); Paselli MD6 (a commercial potato starch maltodextrin with an average DP of 17, Avebe, Antwerpen, Belgium, hereafter referred to as PSMD17); Star-Dri 5 (a commercial waxy maize starch maltodextrin with an average DP of 20, Amylum, Aalst, Belgium, hereafter referred to as WMSMD20);  $\alpha$ - and  $\gamma$ -cyclodextrins (Wacker Chemie GmbH, Glostrup, Denmark, hereafter referred to as CD); and the hereafter-described maltotetraose preparation. More data on PSMD17 and WMSMD20 are given by Defloor et al (1998).

### Preparation of Maltotetraohydrolase (EC 3.2.1.60)

*Pseudomonas stutzeri* NRRL B-3389 was grown as described by Robyt and Ackerman (1971) using 0.1% starch. The ammonium sulfate precipitate (75%) was ultrafiltered (Sartorius, 10,000 Da, 2 bar) and lyophilized.

The maltotetraohydrolase activity was determined with 1% (w/v) soluble starch (Merck) solution buffered with 0.1M sodium phosphate buffer (pH 7.0). One volume of the starch solution and one volume of a properly diluted enzyme solution were incubated at 37°C for 10 min. The reducing value was then determined by a ferricyanide-cyanide color reaction (Hizukuri et al 1981). One unit (U) of activity corresponded to the amount of enzyme that produced 1  $\mu$ mol of reducing sugar per minute at 37°C and pH 7.0.

### Preparation of Maltotetraose

Maltotetraose was produced from waxy maize starch (meriwax E, Amylum). The starch was gelatinized at 100°C (15 min, with stirring) in excess water (20 mL/g of starch) and cooled at room temperature with stirring (15 min). The mixture was shaken at 40°C and enzyme (7.8 U/g of starch) was added. Incubation was for 40 or 120 min. The reaction was stopped by the addition of two volumes of ethanol (Robyt and Ackerman 1972) and centrifugation at 10,000  $\times$  g for 15 min. The ethanol was removed from the supernatant by rotary evaporation at 50°C before lyophilization. Desalting was performed in a batch process with 6.0 g of mixed-bed resin (Bio-Rad, Hercules, CA, AG 501-X8(D) molecular grade) per gram of lyophilisate. A 10.0% solution of lyophilized maltotetraose in milliQ-water was incubated while being shaken with

<sup>1</sup> Biotechnology Laboratory, Department of Civil Engineering, Aalborg University, Sohngaardsholmvej 57, DK-9000 Aalborg, Denmark.

<sup>2</sup> Corresponding author. Phone: +45 96 35 84 63. Fax: +45 98 14 25 55. E-mail: i5lp@civil.auc.dk.

<sup>3</sup> Laboratory of Food Chemistry, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, B-3001 Heverlee, Belgium.

the resin for 15 min at room temperature. The resin was removed from the sample by filtration (0.45  $\mu\text{m}$ , Millipore, Bedford, MA, type HA). The sample was then lyophilized.

### Analysis of Oligosaccharides

The lyophilized maltotetraose was analyzed for protein (Bradford 1976), reducing sugars (Hizukuri et al 1981), and total sugars (Dubois et al 1956). The elution pattern on a prepacked Sephadex 75 HR 10/30 column (Pharmacia Biotech, Uppsala, Sweden) using fast protein liquid chromatography (LKB Pump P-500, Controller Lcc-501 Plus, Pharmacia Biotech) was recorded to check whether any larger dextrans were present. The following standards—Dextran T-10, 1.0 mg/mL (10,000 Da); maltoheptaose, 0.5 mg/mL (Sigma); maltotriose (Fluka); and glucose, 0.4 mg/mL—were applied with a sample loop of 200  $\mu\text{L}$ . Standards and samples were eluted with 0.3% (w/v) NaCl, and collected fractions (0.4 mL) were tested for total sugar (Dubois et al 1956), using glucose standards of 10–200  $\mu\text{g/mL}$ .

Oligosaccharides were analyzed by a high-performance anion exchange chromatography system (Dionex Corp., Sunnyvale, CA) with pulsed amperometric detection. The system was connected to a gradient pump (GP 40), electrochemical detector (ED 40), and an automated sampling system (AS 3500). A linear gradient of 1.0M sodium acetate (Merck, Darmstadt, Germany) ranging from 0 to 60% over 30 min in 100 mM sodium hydroxide (Baker, Deventer, Holland, 50% solution) was applied, with a flow rate of 1.0 mL/min. A CarboPac PA-100 (Dionex) column and a CarboPac PA-100 guard column were used. The total run time for each sample was 50 min. All samples were filtered through a 0.22- $\mu\text{m}$  filter before testing.

### Farinograph Characteristics

A farinograph (Brabender, Duisburg, Germany) with a 50-g mixer was used to evaluate the impact of the material on the water absorption of the flour. Carbohydrates were added as 10.0% (w/v) solutions at 3.0% (based on flour weight) levels. The control contained flour and water without addition of malto-oligosaccharides. Dough consistency and development time were determined, as was dough softening, i.e., the difference in Brabender consistency (in farinograph units [FU]) between the peak value and the value after mixing 12 min beyond the peak value.

### Preparation of Wheat Flour-Water Doughs

Flour (10.0 g, UNO, Ceres, Belgium) was mixed to optimum (130 sec) with a 10-g pin mixer (TMCO-National Manufacturing, Lincoln, NE) with 5.72 ml of water (i.e., resulting in a consistency of 500 FU). When carbohydrate materials were added, this was done with the same amount of water as for the control. To this

**TABLE I**  
Farinograph Values for Water-Flour Doughs Prepared with 57.2% Water Absorption (14% moisture basis) for Dough of 500-FU Consistency

Added Component (3.0% w/w)	Consistency (FU)	Farinograph Water Absorption (%)	Development Time (min)	Mixing Stability (min)	Degree of Softening (FU)
None	508	57.2	2.2	5.1	66
Glucose	539	58.0	2.0	6.0	71
Maltose	543	58.1	1.9	5.5	66
Maltotriose	529	57.7	1.7	5.7	65
Maltotetraose	559	58.5	2.0	4.8	77
$\alpha$ -CD <sup>a</sup>	674	61.4	1.7	4.5	132
$\gamma$ -CD <sup>a</sup>	693	61.8	2.9	5.0	119
PSMD17 <sup>a</sup>	532	57.8	1.7	6.3	62
WMSMD20 <sup>a</sup>	521	57.5	2.0	7.7	54

<sup>a</sup> CD = Cyclodextrin, PSMD17 = potato starch maltodextrin with average degree of polymerization of 17, WMSMD = waxy maize starch maltodextrin with average degree of polymerization of 20.

end, carbohydrate solutions (10%, w/v) were prepared and the amounts added were 1.0 and 3.0% carbohydrate dry matter (based on flour weight).

### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC 120, Seiko, Kawasaki Kanagawa, Japan) was used to investigate the gelatinization of starch and the recrystallization of amylopectin of the baked flour-water dough in the sealed pans. An empty pan was used as a reference. The DSC run was performed at 5–150°C at a heating rate of 4°C/min. The onset temperature ( $T_o$ ), the completion temperature ( $T_c$ ), and the enthalpy ( $\Delta H$ ) of the staling endotherm (melting of crystallized amylopectin) were determined with Seiko software.

Dough samples (16–25 mg) were accurately weighed in five DSC aluminum pans (Seiko, P/N SSC000C009). One sample was immediately measured in the calorimeter (4°C/min, 5–150°C). The remaining four sealed pans were placed in an oven at 105°C for 30 min to “bake” the wheat flour and water dough. Immediately after cooling to room temperature, one sample was measured by DSC to confirm that the starch had gelatinized. Three baked samples were stored at room temperature for seven days. Selected samples were stored at 6°C for 48 hr or at –18°C for 168 hr followed by 120 hr at room temperature before DSC was performed.

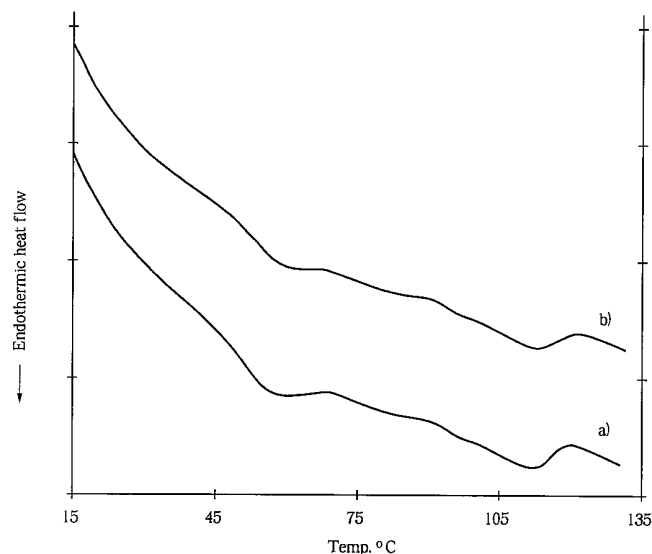
## RESULTS AND DISCUSSION

### Preparation of Maltotetraose

Maltotetraohydrolase (7.8 U/g of starch) added to starch (50 mg/mL) resulted in a yield of 50% (w/w) maltotetraose at 40°C and 120 min. This is higher than the 35% (w/w) yield obtained by incubation for 40 min at 40°C by Robyt and Ackerman (1972). A longer incubation time increased the amounts of maltotriose, maltose, and glucose produced. While the precipitate obtained by ethanol addition contained large starch-derived dextrans, the maltotetraose was recovered from the supernatant. It had a purity of 85% determined by high-performance anion exchange chromatography. Maltotriose was the main side-product.

### Farinograph Characteristics

Farinograph values of the flour-water dough and samples obtained by the addition of 3.0% (w/w) low molecular weight carbohydrates are listed in Table I. Addition of most of the low molecular



**Fig. 1.** Differential scanning calorimetry thermograms of baked and aged wheat flour-water dough containing 3.0%  $\gamma$ -cyclodextrin after storage for seven days at room temperature (b) compared to the control without additions (a).

weight carbohydrates resulted in a small increase in the dough consistency, while increased dough consistencies of 674 and 693 FU were found for  $\alpha$ - and  $\gamma$ -cyclodextrin, respectively. Expressed alternatively, the 500 FU water absorption of the control dough (57.2%) was increased after the addition of cyclodextrins to 61.4% ( $\alpha$ -CD) and 61.8% ( $\gamma$ -CD). An increase in the farinograph water absorption by the addition of  $\beta$ -CD (0.5–1.6%, w/w) to wheat flour dough was previously found by Kim and Hill (1984a). Addition of  $\beta$ -CD increased the development time, as well as the loaf volume of bread. The obtained results showed an increase in development time after the addition of 3.0%  $\gamma$ -CD (from 2.2 to 2.9 min), but not after the addition of  $\alpha$ -CD. Addition of WMSMD20 increased the mixing stability from 5.1 to 7.7 min. The softening of the dough, i.e., the difference in Brabender consistency (FU) between the peak value and the value when mixed 12 min beyond the peak value, was increased by the addition of cyclodextrins (from 66 FU for the control to 132 FU for  $\alpha$ -CD and 119 FU for  $\gamma$ -CD) due to the increased dough consistency following  $\alpha$ -CD and  $\gamma$ -CD addition. The lowest amount of softening was found after the addition of the larger dextrins (WMSMD20 and PSMD17), with 54 and 62 FU, respectively, compared to 66 FU for the control.

### Staling Endotherm

The effects of the low molecular weight carbohydrates on melting of crystallized amylopectin was measured by DSC. A DSC thermogram of the baked and aged flour-water dough after the addition of 3.0%  $\gamma$ -CD and of the control is shown in Fig. 1. The staling-associated endotherm (Eliasson 1985) for crystallized amylopectin melting is seen in the temperature range of 40–70°C. The transition near 100°C has been attributed to the melting of the amylose-lipid complex (Kugimiya et al 1980).

Table II shows the  $\Delta H$  in the temperature range 40–70°C measured by DSC of baked and aged flour-water doughs after the addition of low molecular weight carbohydrates and the average onset and completion temperatures of the endotherms, with the corresponding standard deviations.

**TABLE II**  
Enthalpies ( $\Delta H$ ) of Staling Endotherms of Doughs Prepared with UNO Flour With and Without the Addition of 1.0 or 3.0% Low Molecular Weight Carbohydrates<sup>a</sup>

Added Component	Concentration (%)	$T_o$ (°C)	$T_c$ (°C)	$\Delta H$ (mJ/mg)
None	No addition	47.1 (0.4)	67.9 (0.6)	1.9 (0.2)
Glucose	3	46.7 (0.6) <sup>b</sup>	68.2 (0.3) <sup>b</sup>	2.0 (0.2) <sup>b</sup>
	1	47.9 (0.2)	68.8 (0.3)	1.8 (0.1)
Maltose	3	47.0 (0.4)	68.2 (0.3)	1.9 (0.2)
	1	47.9 (0.4)	68.6 (1.0)	1.6 (0.2)
Maltotriose	3	48.7 (0.5)	69.0 (0.1)	1.9 (0.2)
	1	48.3 (0.4)	68.4 (0.8)	2.0 (0.1)
Maltotetraose	3	46.7 (0.2)	68.2 (0.2)	2.1 (0.1)
	2	46.8 (0.2)	68.2 (0.4)	2.1 (0.3)
	1	47.1 (0.8)	68.7 (1.2)	2.1 (0.2)
$\alpha$ -CD <sup>c</sup>	3	48.6 (0.4)	69.1 (0.3)	1.8 (0.1)
	1	48.1 (0.8)	68.2 (0.4)	1.8 (0.1)
$\gamma$ -CD	3	48.3 (0.3)	67.5 (0.2)	1.2 (0.2) <sup>d</sup>
	1	48.8 (0.2)	68.2 (0.2)	1.6 (0.1)
PSMD17 <sup>c</sup>	3	46.6 (0.8)	69.1 (0.3)	1.8 (0.0)
	1	46.7 <sup>e</sup>	69.3 <sup>e</sup>	2.0 <sup>e</sup>
WMSMD20 <sup>c</sup>	3	47.8 (0.8)	69.3 (1.1)	1.8 (0.1)
	1	46.4 <sup>e</sup>	69.5 <sup>e</sup>	2.0 <sup>e</sup>

<sup>a</sup> Average onset ( $T_o$ ) and completion ( $T_c$ ) temperatures are shown with the standard deviations (in parentheses). Unless otherwise indicated, three replicates were run.

<sup>b</sup> Four determinations.

<sup>c</sup> CD = cyclodextrin, PSMD17 = potato starch maltodextrin with average degree of polymerization of 17, WMSMD = waxy maize starch maltodextrin with average degree of polymerization of 20.

<sup>d</sup> Significant lower than the baked and aged dough with no addition (unpaired *t*-test,  $\alpha = 0.05$ ).

<sup>e</sup> Two determinations.

The  $\Delta H$  of the baked and aged flour-water dough containing 3.0%  $\gamma$ -CD is significantly lower than that of the baked and aged control (unpaired *t*-test,  $\alpha = 0.05$ ). None of the baked and aged flour-water doughs containing linear maltooligosaccharides decreased the  $\Delta H$  of the melting of the crystallized amylopectin. Enthalpies obtained after the addition of PSMD17 or WMSMD20 indicate that the maltodextrin source did not influence the results. In contrast, Defloor and Delcour (*in press*) in similar experiments with a different flour found that the two starch-derived maltodextrins statistically decreased the same endotherm. However, in their experiments, flour-water doughs of a constant (600 FU) consistency were used, while in the present work, doughs of constant water absorption (57.2%) were prepared.

It follows from the above that, in our work, malto-oligosaccharides, independent of their size, had no effect on amylopectin recrystallization. Assuming that bread firming corresponds to amylopectin recrystallization, our results are in accordance with those of Every et al (1992), who reported that the bread firming rate is unaffected by the addition of dextrins. Also, Lin and Lineback (1990) found that the presence of extracted linear maltooligosaccharides from dough could not be correlated with the firming rate of bread. Salem and Johnson (1965) also found that additions of glucose and maltose (1.0%, w/w) had no effect on bread firming. The addition of 1.0, 2.0, and 3.0% (w/w) sucrose also did not affect the staling endotherm (Defloor and Delcour, *in press*). The results for these low molecular weight carbohydrates correlate with the findings here.

Storage at 6°C for 48 hr before incubation at room temperature (120 hr) resulted in increased  $\Delta H$  for baked and aged flour-water doughs (Table III). The onset and completion temperatures were lower (44 and 64°C, respectively) than after seven days at room temperature (47 and 68°C, respectively). Increased nucleation of starch stored at 6°C has been reported to result in increased propagation (development of the crystallinity) at room temperature (Levine and Slade 1990). This may explain the larger endotherm values obtained upon melting of the crystallized amylopectin. The decreased  $\Delta H$  after the addition of 3.0%  $\gamma$ -CD and storage at room temperature was not detected following incubation at 6°C for 48 hr. DSC analysis of samples incubated in the freezer (–18°C) for seven days did not show a staling endotherm.

The structure of the cyclodextrins may account for the observed differences in the melting of the crystallized amylopectin and the farinograph characteristics. Kim and Hill (1984b) suggested that  $\beta$ -CD interacts with lipids, thereby affecting the viscosity of starch pastes. A similar interaction may have affected the farinograph characteristics. Interactions between  $\beta$ -CD and components other than starch granules in the wheat flour dough have also been suggested by Kim and Hill (1984b). The results obtained indicate that the effect of  $\alpha$ -CD on amylopectin crystallization is lower than that of  $\gamma$ -CD. This may result from the larger size of  $\gamma$ -CD.

In this work, only  $\gamma$ -CD was able to reduce the staling endotherm of a baked wheat flour-water dough. The results indicate

**TABLE III**  
Influence of Storage Conditions on the Enthalpy ( $\Delta H$ ) of the Staling Endotherm of Baked and Aged Doughs Containing 3.0% Maltotetraose or  $\gamma$ -Cyclodextrin ( $\gamma$ -CD)<sup>a</sup>

Added Component	Storage Conditions <sup>b</sup>	$T_o$ (°C)	$T_c$ (°C)	$\Delta H$ (mJ/mg)
None	A	47.1 (0.3) <sup>c</sup>	68.5 (0.9) <sup>c</sup>	2.0 (0.2) <sup>c</sup>
	B	44.8 (0.2) <sup>c</sup>	64.8 (0.4) <sup>c</sup>	3.2 (0.2) <sup>c</sup>
Maltotetraose 3%	A	46.3	61.6	2.0
	B	44.5	64.9	3.3
$\gamma$ -CD, 3%	A	47.4	68.8	1.5
	B	44.9	64.8	3.4

<sup>a</sup> Two replicates were run unless otherwise indicated.

<sup>b</sup> A = 168 hr at room temperature, B = 48 hr at 6°C followed by 120 hr at room temperature.

<sup>c</sup> Five determinations

that the other carbohydrates tested do not have a direct effect on staling. It is therefore tempting to conclude that the antistaling effect exerted by  $\alpha$ -amylase in breadbaking is due to a modification of the starch structure, as concluded by Gerrard et al (1997) rather than to the size of the carbohydrates formed. However, findings by Every et al (1992), Lin and Lineback (1990), and Martin and Hosenev (1991) necessitate some caution when conclusions are drawn. The observations by Every et al (1992) that the addition of maltodextrins of DP 3–10 leaves the crumb firming rate unaffected, while at the same time there is a relationship between the level of extractable dextrans and the crumb softness, indicate the complexity of the system. These observations, taken together with the findings of Martin and Hosenev (1991) that firming is retarded in bread supplemented with  $\alpha$ -amylase producing linear oligosaccharides, and the antistaling effect of the produced branched-chain products found by Lin and Lineback (1990) make interpretation rather difficult. Although it seems obvious that retrogradation of starch would be affected by its structure, it may well be that the maltodextrins formed by the enzymatic action are present where and when needed to influence starch retrogradation. In contrast, added dextrans may be more prone to  $\beta$ -amylolysis because they are already present at the dough-making stage. In this respect, it is important to note that  $\beta$ -amylase is less heat stable than many amylases used in breadmaking.

In summary, the addition of  $\alpha$ - and  $\gamma$ -CD to wheat flour-water dough increased the dough consistency. Decreased melting of the crystallized amylopectin after the addition of 3.0%  $\gamma$ -CD (based on flour weight) to baked and aged wheat flour-water dough was detected by DSC. Addition of low molecular weight carbohydrates did not have a significant effect on the melting of crystallized amylopectin after seven days of storage. Further work is needed, however, to establish the major interaction of cyclodextrins and branched dextrans in the complex dough system.

#### ACKNOWLEDGMENT

We thank Aalborg University for financial support, L. H. Pedersen (Aalborg University) for supplying maltotetrahydrolase, and Isabelle Defloor (Katholieke Universiteit, Leuven) for practical advice and helpful discussions.

#### LITERATURE CITED

- Bradford, M. M. 1976. A rapid method for the quantitation of microgram quantities of protein utilising the principle of protein-dye binding. *Anal. Biochem.* 72:248-254.
- Defloor, I., and Delcour, J. A. *In press*. The impact of maltodextrins and antistaling enzymes on the DSC endotherm of baked doughs. *J. Agric. Food. Chem.*
- Defloor, I., Vandenreyken, V., Grobet, P. J., and Delcour, J. A. 1998. Fractionation of maltodextrins by ethanol. *J. Chromatogr. A* 803:103-109.
- Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., and Smith, F. 1956. Colorimetric method for determination of sugars and related substances. *Anal. Chem.* 28:350-356.
- Eliasson, A.-C. 1985. Retrogradation of starch as measured by differential scanning calorimetry. Pages 93-98 in: *New Approaches to Research on Cereal Carbohydrates*. R. D. Hill and R. D. Munck, eds. Elsevier Science: Amsterdam.
- Every, D., Mann, J. D., and Ross, M. 1992. The relationship of dextrans in bread to staling and crumb gumminess. Pages 179-186 in: *Proc. Australian Cereal Chemistry Conference*, 42nd. V. J. Humphrey-Taylor, ed. RACI: Melbourne.
- Gerrard, J. A., Every, D., Sutton, K. H., and Gilpin, M. J. 1997. The role of maltodextrins in the staling of bread. *J. Cereal. Sci.* 26:201-209.
- Hizukuri, S., Takeda, Y., Yasuda, M., and Suzuki, A. 1981. Multi-branched nature of amylose and the action of debranching enzymes. *Carbohydr. Res.* 94:205-213.
- Kim, H. O., and Hill, R. D. 1984a. Modification of wheat flour dough characteristics by cycloheptaamylose. *Cereal Chem.* 61:406-409.
- Kim, H. O., and Hill, R. D. 1984b. Physical characteristics of wheat starch granule gelatinization in the presence of cycloheptaamylose. *Cereal Chem.* 61:432-435.
- Kugimiya, M., Donovan, J. W., and Wong, R. Y. 1980. Phase transitions of amylose-lipid complexes in starches: A calorimetric study. *Starch/Staerke* 32:265-270.
- Levine, H., and Slade, L. 1990. Influences of the glassy and rubbery states on the thermal, mechanical, and structural properties of doughs and baked products. Pages 157-331 in: *Dough Rheology and Baked Product Texture*. H. Faridi and J. M. Faubion, eds. Van Nostrand Reinhold: New York.
- Lin, W., and Lineback, D. R. 1990. Changes in carbohydrate fractions in enzyme-supplemented bread and the potential relationship to staling. *Starch/Staerke* 42:385-394.
- Martin, M. L., and Hosenev, R. C. 1991. A mechanism of bread firming. II. Role of starch hydrolyzing enzymes. *Cereal Chem.* 68:503-507.
- Robyt, J. F., and Ackerman, R. J. 1971. Isolation, purification, and characterisation of a maltotetraose producing amylase from *Pseudomonas stutzeri*. *Arch. Biochem. Biophys.* 145:105-114.
- Robyt, J. F., and Ackerman, R. J. 1972. Amylase from *Pseudomonas stutzeri*. *Methods Enzymol.* 28:925-930.
- Salem, A. E., and Johnson, J. A. 1965. Influence of various oligosaccharides on staling of bread. *Food Technol.* 19:167-170.
- Schenck, F. W., and Hebeda, R. E. 1992. Oligosaccharides: production, properties and applications. Pages 335-366 in: *Starch Hydrolysis Products*. Worldwide Technology, Production and Applications. M. Okada and T. Nakakuki, eds. VCH Publishers: New York.
- Schoch, T. J., and French, D. 1947. Studies on bread staling. I. The role of starch. *Cereal Chem.* 24:231-249.

[Received August 7, 1998. Accepted December 6, 1998.]