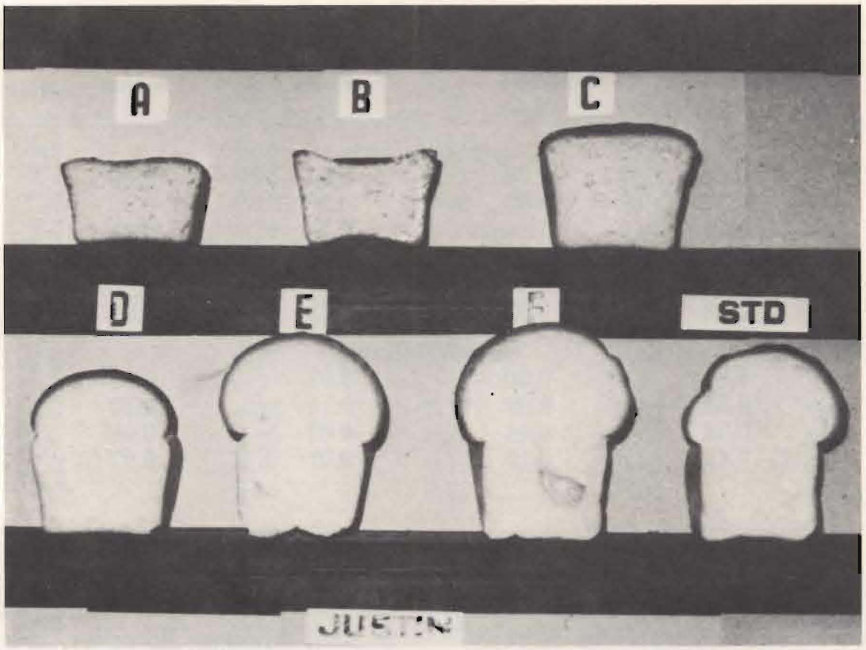

Figure 1. Photograph showing the effect of wheat maturation on bread quality (macro milled flour—Justin variety). A. 16 days pre-ripe; B. 13 days pre-ripe; C. 9 days pre-ripe; D. 6 days pre-ripe; E. 3 days pre-ripe; F. ripe and standard flour (internal view).

The Importance of Carbohydrates In Relation To Milling and Baking

Bert L. D'Appolonia

Although the gluten proteins of wheat flour are of prime importance to produce a high quality loaf of bread, the carbohydrates also serve specific functions. Work in carbohydrates at the Department of Cereal Chemistry and Technology has been conducted in several areas in an attempt to elucidate structures and ascertain the importance of this biochemical constituent in wheat quality.

Carbohydrates represent a major component of wheat and wheat flour and include the free sugars, the glucofructans, the pentosans and starch. Carbohydrates serve specific functions in physical dough properties as well as in bread baking. The following report will discuss primarily some of the studies conducted in the area of carbohydrates in the Department of Cereal Chemistry and Technology.

Sugars

The amount of sugars present in wheat flour is generally low, with values of between 1 and 2 per cent often being reported. In bread baking, these sugars are used up by the fermentation process, and sugar is generally added in the bread baking formula because of the low amounts present. Free sugars normally found in wheat flour include sucrose, maltose, raffinose, fructose and glucose.

In one study (1), the changes in carbohydrate components during wheat maturation were followed, and more specifically, the change in free sugars. Table 1 shows some of the results obtained for a hard red spring and durum wheat variety. Sucrose, fructose and glucose contents decreased as the wheat matured. Raffinose, a trisaccharide, appeared only at the later stages of wheat development. Small differences in amount of maltose were noted at the different levels of maturity. The presence of maltose has generally been attributed to the autolysis of starch or similar polysaccharides, or it may be formed by transglucosidation.

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Table 1. Free sugars in maturing wheat.[1]

Original moisture %	Sucrose %	Raffinose %	Maltose %	Fructose %	Glucose %
		HRS (Justin, 1970)			
76.0	0.65	0.00	0.20	3.10	1.54
66.9	0.36	0.00	0.18	0.90	0.75
52.8	0.36	Trace	0.10	0.11	0.18
43.2	0.32	0.04	0.10	0.06	0.14
31.1	0.18	0.04	0.07	0.04	0.09
17.9	0.08	0.03	0.03	0.01	0.05
		Durum (Leeds, 1969)			
74.0	0.84	0.00	0.07	0.94	0.75
61.4	0.31	0.00	0.10	0.10	0.31
46.1	0.34	0.09	0.08	0.08	0.12
39.9	0.41	0.19	0.07	0.07	0.10

[1] *At 14.0% moisture basis.*

Table 2 shows the change in total reducing and nonreducing sugars in the maturing wheat kernel. Reducing sugars showed a steady decrease as the wheat matured for both the hard red spring and durum wheat varieties, whereas the amount of nonreducing sugars revealed a fluctuation in the values at the different stages of maturity.

The higher sugar content in immature wheat flour is readily noticeable if one bakes bread from such flour (2). Extremely dark crust color can be noted with the extremely immature wheat due to the large concentrations of sugars and water-solubles. Crumb color also improved with maturity. The color ranged from dark green at the early stages of maturity to light yellow at nine days pre-ripe, to a creamy color at the final stages of maturity (Figure 1). Improvement in bread quality with maturation is very evident.

Another study (11) involved examination of the free sugars present in different mill streams obtained from a pilot mill, as well as in pin milled and air classified flour fractions. The protein shift that occurs with pin milling and air classification is well known; however, what happens to the carbohydrates is not as well known. The purpose of this study, therefore, was to investigate the sugars in the unfractionated flour and the pin-milled and air classified flour fractions obtained from different mill streams of four different wheat varieties.

Table 2. Total reducing and nonreducing sugars in maturing wheat kernel.

Original moisture %	Reducing sugars[1,2] mg./kernel	Nonreducing sugars[1,3] mg./kernel
	HRS (Justin, 1969)	
70.0	0.53	0.74
58.0	0.29	0.37
49.3	0.29	0.45
28.0	0.15	0.45
12.5	0.06	0.44
9.9	0.05	0.21
	Durum (Leeds, 1969)	
64.0	0.43	0.53
54.4	0.29	0.58
44.1	0.21	0.56
13.8	0.12	0.30
9.7	0.12	0.46

[1] *At 14.0% moisture basis.*
[2] *Expressed as maltose.*
[3] *Expressed as sucrose.*

In addition to the unfractionated flours, three fractions were analyzed: fine-1 (F-1) (high-protein flour), fine-2 (F-2) (low-protein flour), and coarse-2 (C-2) intermediate protein flour. The high protein containing fraction for all flour streams of the four varieties contained the highest amount of total sugar, and reducing and nonreducing sugars. Table 3 shows that this fraction also contained the highest amounts of the individual free sugars, sucrose and raffinose.

Pin milling and air classification caused displacement of sucrose, raffinose and possibly maltose. Total sugars present in the low and intermediate protein containing fractions, in general, was similar to that present in the original flour.

More total sugar was found in the break flour streams than in the middling flour streams due to the higher sugar content present in the bran than in the endosperm. This was also evident for sucrose content.

Glucofructans

Glucofructans present in wheat flour (about 1 per cent) represent a group of water-soluble nonreducing carbohydrates which extend in molecular size from sucrose to polysaccharides with molecular weights of around 2000. The glucofructans have not displayed any really significant roles in milling or in dough properties or baking. Their main role in baking is probably as a source of food for the yeast during fermentation.

Table 3. Individual sugar analysis[1] (Waldron variety).

Flour stream	Fraction	Sucrose %	Raffinose %	Maltose %	Fructose %	Glucose %
2M	Unf.	0.19	0.06	0.06	0.02	0.05
	F-1	0.25	0.10	0.05	0.02	0.04
	C-2	0.13	0.03	0.04	0.03	0.04
	F-2	0.16	0.05	0.06	0.04	0.05
2B	Unf.	0.17	0.06	0.03	0.02	0.04
	F-1	0.28	0.13	0.06	0.02	0.05
	C-2	0.14	0.05	0.05	0.02	0.04
	F-2	0.17	0.05	0.06	0.03	0.05
5B	Unf.	0.34	0.17	0.02	0.03	0.08
	F-1	0.45	0.27	0.06	0.02	0.05
	C-2	0.27	0.11	0.03	0.02	0.04
	F-2	0.34	0.18	0.04	0.02	0.04
T	Unf.	0.33	0.15	0.05	0.03	0.06
	F-1	0.47	0.28	0.06	0.02	0.05
	C-2	0.23	0.09	0.06	0.03	0.05
	F-2	0.31	0.13	0.06	0.03	0.05

[1] *Results expressed on a dry basis.*

Pentosans

Pentosans, a polysaccharide material in wheat flour, represent a minor component. However, because of certain properties they possess, they have been investigated extensively. The average baker's patent flour contains 2 to 3 per cent total pentosans. Those extractable with water from flour are also referred to as "gums". Those associated with the "tailings", "sludge" or amylodextrin fraction of wheat flour are referred to as hemicelluloses, or the water-insoluble endosperm pentosans. Once extracted, however, they are water-soluble.

Attempts have been made in the past to establish a correlation between ash and pentosan content of flours. Generally, low pentosan was associated with low ash content. In measuring the pentosan content of flour that has been pin milled and air classified, it has been found in some of our work that the high protein containing fraction contains the highest pentosan content.

In the isolation of water-soluble pentosans from wheat flour, considerable protein material as well as soluble starch material is generally found associated with the pentosan. Therefore, purification and fractionation is required before obtaining an essentially pure pentosan fraction. In the laboratory, the extractable pentosan material is treated with alpha amylase to remove the soluble starch material, followed by fractionation on DEAE-cellulose (borate form) to fractionate the pentosans into five fractions. The first two fractions are essentially pure pentosans, while the remaining fractions contain considerable amounts of protein as well as the sugar galactose.

This technique has been utilized to investigate the effect of pentosans in bread baking (5). Certain studies utilizing crude pentosans to examine their effect in bread baking are highly questionable due to the presence of considerable amounts of protein material.

Table 4 shows some of the results obtained in bread baking using the various DEAE-cellulose pentosan fractions. Again, it is important to remember that the pure pentosan fractions are fractions 1 and 2. From this table it can be noted that the addition of total water-solubles or the crude or amylase treated pentosans had an improving effect on loaf volume. However, the addition of F_1 and F_2 combined showed practically no effect on loaf volume and had a detrimental effect on crust color. The addition of the DEAE-cellulose pentosan fractions which contained protein had an improving effect on loaf volume. This study would indicate that it is the protein associated with the pentosan that was responsible for increasing the loaf volume.

The exact role of pentosans in baking, however, is still not entirely clear or understood. Recent studies (4) reported a dramatic effect on volume of bread produced from non-wheat crops that resulted from the addition of a pentosan preparation. The ability of pentosans to bind a considerable amount of water is extremely important. This results in increasing the amount of water used in bread baking. This property of pentosans is well documented.

The pentosans extracted from conventional and continuous bread after different days of stor-

Table 4. Effect of water-solubles, pentosans, and fractionated pentosans extracted from HRS (Thatcher and Justin) flours on gluten-starch loaves.[1]

Addition	Thatcher				Justin			
	Loaf volume		Crust color		Loaf volume		Crust color	
	I cc.	II cc.	I cc.	II cc.	I cc.	II cc.	I cc.	II cc.
Control (gluten-starch)	127	132	2	2	128	135	2	2
0.8 g. Water-solubles	191	188	3	3	189	170	3	3
0.2 g. Water-solubles	138	155	2+	3	149	148	3	2+
0.2 g. Crude pentosans	142	147	2—	2—	147	154	3	2+
0.2 g. Amylase-treated pentosans	146	145	2—	2—	135	154	2+	2+
0.2 g. F1 + F2B	135	135	1+	1+	137	136	1+	2+
0.2 g. F3 + F4	147	144	2+	2	135	160	2	3
0.2 g. F4 + F5	153	151	3	2+	158	165	3	2+

[1] *I and II refer to duplicate bakes.*

age also have been examined (8). This study indicated that there does not appear to be any major change in the pentosans of wheat flour when processed into either conventional or continuous bread.

Table 5 shows that the amount of crude pentosans isolated from the continuous bread crumb was greater than that extracted from the conventional bread crumb. Protein content increased from day 1 to 9, while the amount of crude pentosans decreased as the bread aged. Considering the protein content, there was a decrease in extractable carbohydrate material as the bread aged, which was probably due to retrogradation of the amylopectin fraction.

The protein content of the amylase-treated pentosans from the continuous crumb or crust was higher in all cases than from the conventional crumb or crust. When the protein material extracted was subtracted from the yield of amylase-treated pentosans, the remaining product recovered, which would be predominantly pentosan material, was similar in all cases.

In addition to water-soluble pentosans and pentosans present in the tailings or sludge fraction of wheat flour, a small amount of pentosan material was associated with the gluten fraction of wheat flour (6).

Table 6 shows the pentosan content in a number of different glutens isolated from hard red spring wheat and durum wheat. Pentosan content was higher in the durum wheat glutens. Results appeared to indicate that the pentosans associated with gluten are similar to the pentosans extracted from flour by water. This pentosan material associated with the gluten could very well be of extreme importance in affecting physical dough properties. The problem involved in such an investigation is that extraction of the pentosan normally involves alkaline extraction and thus causes denaturation of the gluten.

Table 5. Data for crude and amylase-treated pentosans from conventional and continuous bread.

	Crude pentosans				Amylase-treated pentosans			
	Crumb		Crust		Crumb		Crust	
Day	Recovery %	Protein[1] %	Recovery %	Protein[1] %	Recovery %	Protein[1] %	Recovery %	Protein[1] %
					Conventional bread			
1	1.6	12.9	2.2	9.1	0.68	9.8	0.72	10.2
4	1.9	11.9	2.5	9.6	0.71	4.8	0.77	5.2
7	1.1	25.0	2.1	13.5	0.70	6.5	0.84	5.1
9	1.1	25.4	—	—	0.69	5.0	—	—
					Continuous bread			
1	2.7	11.3	2.4	8.7	0.76	17.5	0.65	15.3
4	2.5	11.9	2.6	11.5	0.89	21.3	0.80	14.5
7	2.1	16.6	2.1	11.3	0.76	22.2	0.73	19.9
9	2.4	17.5	2.5	10.3	0.88	21.4	0.76	19.0

[1] *Expressed on a dry basis.*

Table 6. Protein and pentosan content of different glutens.

Gluten source	Protein %	Pentosans %	Gluten source	Protein %	Pentosans %
HRS			Durum		
Chris	76.7	1.86	Durum composite	66.5	2.68
1812	76.7	1.76	Wells	73.9	2.72
Semidwarf	80.3	1.17	Leeds	80.0	2.20
Chris[1]	78.4	1.78	Mindum	80.5	2.03
Red River 68	78.1	1.95			

[1] *The two Chris varieties were grown at different locations.*

One important property of pentosans is their ability to form a gel in the presence of an oxidizing agent (13). Work has been reported indicating that the substance was a glycoprotein containing ferulic acid. Also reported was that DEAE-cellulose fraction 2 was responsible for the gelation.

More recent work, however, has been conducted involving rechromatography on a DEAE-cellulose column of the gel-forming glycoprotein fraction containing ferulic acid (12). This study showed that this fraction was actually a mixture of three components. A protein-free polysaccharide fraction containing ferulic acid had the gel-forming property upon oxidation with H_2O_2.

Such a property could be of extreme importance in physical properties of the dough and in bread baking.

Starch

Starch is the most abundant biochemical constituent in wheat flour. The amount of starch present depends on the type of wheat and type of flour, but in general patent flour on a dry basis is about 75-80 per cent starch.

Starch is made up of two components, the linear chain amylose and the branched chain amylopectin. It exists in the form of distinct granules, with the size of the granules being characteristic of a particular cereal.

Figure 2 shows photographs of starch granules isolated from hard red spring wheat, durum wheat, rye and triticale (3). The difference in size and shape of the granules is readily apparent.

The granule is of particular importance during the milling operation, since damage to the starch during wheat flour milling affects the dough properties and the baked loaves prepared from it. Generally, a moderate amount of damaged starch is beneficial, but excessive damage is undesirable. As the amount of starch damage is increased, a greater amount of hydrolysis by the

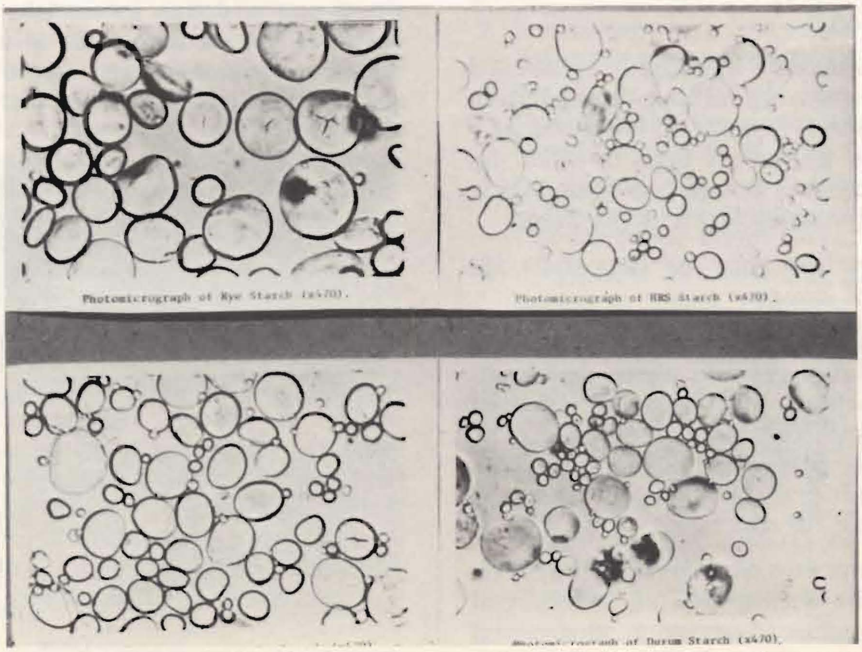

Figure 2. Photomicrographs of different starch granules. Magnification (X 470). Lower left: Triticale; lower right: durum; upper left: rye; upper right: HRS.

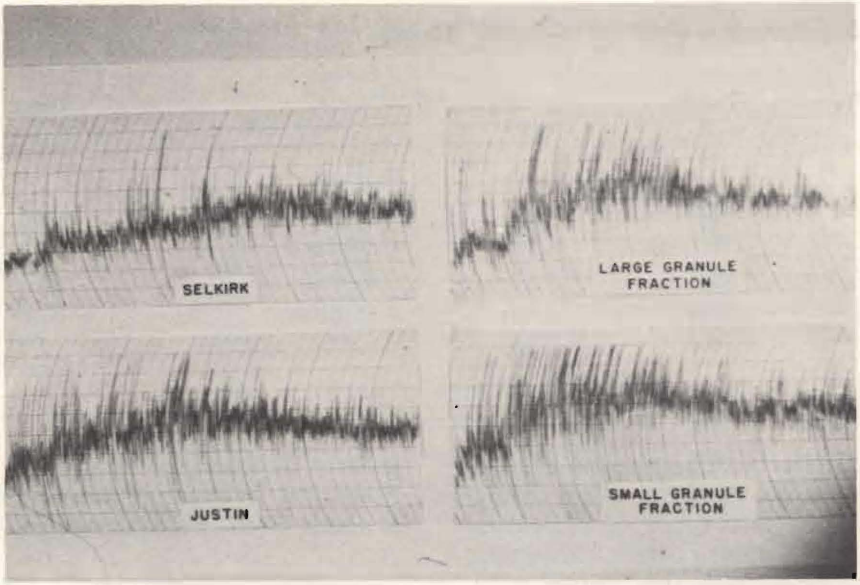

Figure 3. Mixograph curves showing the effect of granule size on mixing characteristics.

amylase enzymes takes place and thus more starch is broken down. If damage is excessive, the resultant bread is of inferior volume, has a gray soggy crumb and a dark crust. Under the same milling conditions, flour from hard wheat generally has more damaged granules than flour from soft wheat. Damage generally increases with the protein content of hard wheat. Damaged starch increases the water absorption of a flour as well as the amount of fermentable sugar.

Starches from different varieties of wheat vary greatly in baking quality. However, wheat starch generally is superior in baking quality over starches from other plant species. Rice, corn, waxy corn and potato starches do not have the baking quality of wheat starch.

Starch granules become thoroughly embedded in the gluten matrix during mixing. Immediately after mixing, the starch is more or less randomly oriented within the gluten. It may be that the starch and gluten become bound together during mixing by relatively strong electrostatic forces.

Size of the granules may be important for mixing properties of dough.

Figure 3 shows mixing curves obtained with the mixograph for large granule starch and small granule starch fractions and using a common gluten substrate and constant absorption. The starches with a larger proportion of small granules (Justin and the small granule fraction) appear to have stronger mixing curves.

Figure 4 shows mixograph curves obtained on starch-gluten systems with untreated commercial corn and wheat starches. A common gluten and constant absorption were used. The curve with corn starch is much weaker. Apparently, the corn starch granules and gluten do not form a strong cohesive bond. Lipids present in starch may also play an important role.

Amylase enzymes act on the damaged starch granules during fermentation and the function is well known. However, the starch granules within the gluten film also become more highly oriented. This orientation contributes to the strength of the cells which form during fermentation. Again, this suggests a strong adhesion between starch and gluten.

During baking, the gelatinization properties of starch play an important role. Gelatinization is limited because of the limited water present. As the starch in dough gelatinizes during baking the amylases act on the starch at a higher rate until they become inactivated. Various baking ingredients may play a role on the starch pasting properties (9).

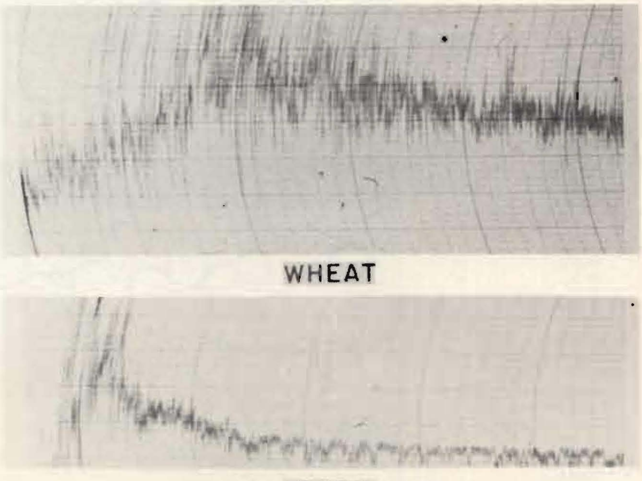

Figure 4. Mixograph curves obtained with wheat and corn starch and common source of gluten.

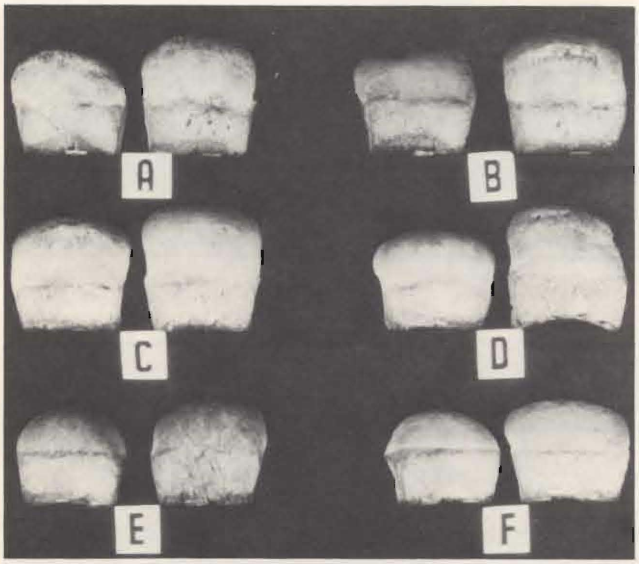

Figure 5. Photograph showing interior and exterior of gluten-starch and gluten-starch-water-soluble loaves. Gluten-starch loaf to the left, gluten-starch-water-soluble loaf to the right, for each pair. Starch source: A. Nugaines, B. Omar, C. Moro, D. large-granule fraction, E. small-granule fraction, F. corn.

Figure 5 shows the exterior of gluten-starch and gluten-starch-water soluble loaves utilizing a common lot of gluten and different starches. Different starches do affect the bread obtained (7).

A most important consideration about starch is its relation to bread staling. Staling can occur without loss of moisture. When the original moisture is retained, the stale crumb regains its fresh characteristics when heated to 60°C or higher.

Although starch retrogradation does not explain all the changes which occur during staling, it is now generally recognized as the most important single factor. Both bread and starch pastes become firmer with age, both decrease in ability to swell in cold water, in amount of soluble starch which can be extracted by water, and in susceptibility to amylase action. The change in x-ray pattern with bread staling has been studied by several investigators. Bread staling is most probably due to a slow type of retrogradation of the amylopectin fraction of starch. Work is now underway in the Department of Cereal Chemistry and Technology to investigate in some detail the problem of bread staling.

With the introduction of semidwarf wheats into North Dakota, a study was conducted to compare the starch, pentosans and sugars of some conventional height and semidwarf hard red spring wheat flours (10). Small differences were noted in the pasting properties, water-binding capacity values and starch damage values of the starches isolated from the different samples. No extreme differences were noted in the amounts of the various sugars in the different flours.

In general, the results of this investigation have indicated that of the particular carbohydrate properties investigated it would not be possible to separate the conventional-height wheat varieties from the semidwarf samples by any one particular character measured. Certain differences in carbohydrates were noted between varieties. However, the differences were not always between the conventional-height samples and the semidwarf samples, but existed also among the conventional-height varieties and among the semidwarf wheat varieties.

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