Changes in Carbohydrate Components during Wheat Maturation[1]. I. Changes in Free Sugars

M. ABOU-GUENDIA and B. L. D'APPOLONIA[2], North Dakota State University, Fargo 58102

ABSTRACT

Test weight and 1,000-kernel weight increased in hard red spring and durum wheats as the wheat matured and as the original moisture decreased. Reducing and nonreducing sugars in the whole wheat, flour, or semolina decreased as the sample matured. The amount of nonreducing sugars was higher than the amount of reducing sugars at any stage of maturity. The bran, in all cases, contained higher amounts of both reducing and nonreducing sugars than did the corresponding flour or semolina. The total sugar content in the bran, likewise, decreased with maturation of the kernel. Significant correlations were obtained when either reducing or nonreducing sugars in the whole wheat were correlated with percent original moisture and 1,000-kernel weight, respectively. Ion-exchange chromatography revealed that at the early stages of maturity, fructose, sucrose, and glucose were the principal predominant simple sugars in the flour extract. The amount of fructose present in flour or semolina decreased markedly as the grain matured. The glucose content also decreased. Raffinose, a trisaccharide, was detected only at the later stages of development. Small changes were noticeable in maltose content in the flour or semolina at the different levels of maturity. The amount of sucrose initially increased in content and later decreased. The changes in fructose, glucose, sucrose, and raffinose paralleled the changes in reducing and nonreducing sugars, which in turn paralleled the changes in the moisture content of the endosperm during the stages of maturity.

Several reports have appeared in the literature investigating the free mono-, di-, and trisaccharides in wheat and wheat products (1,2,3,4). Owing to the diversity of the methods used in determining the free sugars, and to other factors such as the variable environmental conditions during the growing of wheats, variations in the results were obtained.

In the early studies involving carbohydrate translocation, Bailey (5), McCalla (6), and Miller (7) showed that sugars move into the kernel from the glumes, leaves, and stems until the moisture content falls to about 40%, when translocation ceases. Sugars are converted to starch while the desiccation of the kernel takes place.

Menger (3), using paper chromatography and the ferricyanide procedure, reported that in a durum variety grown under greenhouse conditions, the total reducing sugars decreased by about 92%, whereas the total nonreducing sugars decreased by about 53%, during the period of kernel development. This worker also reported that the raffinose content of the kernel remained relatively constant during the same period, while sucrose, maltose, glucose, and fructose decreased remarkably during maturation. Matsushita (8), using paper chromatography and the glucose-oxidase method, reported that raffinose appeared only at the later stages of maturity, whereas sucrose, fructose, glucose, and maltose decreased with maturity.

[1]Presented at the 56th Annual Meeting, Dallas, October 1971. Published with the approval of the Director of the Agricultural Experiment Station, North Dakota State University, Fargo, as Journal Series No.332. Taken in part from a thesis submitted by M. Abou-Guendia to the North Dakota State University, in partial fulfillment of the requirements for the Ph.D. degree.

[2]Respectively, Graduate Research Assistant, and Assistant Professor, Department of Cereal Chemistry and Technology.

In a detailed study of the changes in carbohydrates and nitrogenous components during maturation of wheat, Jennings and Morton (9) tried to elucidate the relationship between starch, reducing sugars, sucrose, and pentosans. They reported that reducing sugars disappeared almost completely during the maturation phase. They also concluded that reducing sugars and sucrose make a significant contribution to the dry weight of the endosperm. The initial marked decline in reducing sugars and sucrose when rapid starch synthesis was initiated indicated that starch synthesis depletes the pool of precursor compounds and, subsequently, the pool was maintained at the relatively constant level necessary for continued starch synthesis.

Changes in carbohydrate composition during maturation of cereals other than wheat have been reported by other workers, including Harris and MacWilliam (1,10), Merritt and Walker (11), and MacGregor et al. (12).

Owing to considerable disagreement in the literature (1,2,3,4) regarding the kinds and amounts of free sugars present in wheat flour or semolina, and the availability of ion-exchange chromatography (13,14,15) as a new technique for the rapid quantitative determination of carbohydrates, this study was initiated.

The present investigation was conducted to measure the total reducing and nonreducing sugars, as well as mono-, di-, and trisaccharides present in the flour or semolina extracted from hard red spring (HRS) or durum wheat grown under the same environmental conditions and collected at different stages of maturity. Relations between the changes in sugar content of the flour or semolina as the wheat matured and factors such as moisture content, 1,000-kernel weight, and starch content in the flour or semolina measured by the polarimetric procedure (16) were also examined.

MATERIALS AND METHODS

Samples

Two varieties of HRS wheat (Justin and Manitou) and two varieties of durum wheat (Leeds and Lakota) were used for this study. All varieties were grown under field conditions in Casselton, N.D., during two consecutive years, 1969 and 1970.

Samples of each variety were collected at nine different stages of maturity during the 1969 crop year. However, with the 1970 crop, severe hail conditions during the growing period caused destruction of the wheat crop before complete maturation. As a result, only samples at the six initial stages of maturity were collected for the durum wheat. The samples collected were frozen immediately and stored at -23°C., then freeze-dried to a moisture content of 6 to 8%.

Moisture of Harvested Wheat Kernels

Moisture content of the wheat kernels was determined immediately after harvesting with a Brabender moisture meter. Two-gram samples of hand-separated kernels were heated in an oven for 2 hr. at 130°C., and their loss in weight was determined. Results reported were an average of two determinations. Results obtained by this method were similar to those obtained by the modified two-stage air-oven method (16) and, consequently, were used in place of the latter.

Test Weight, 1,000-Kernel Weight, and Kernel Size Distribution

These tests were performed according to AACC Approved Methods (16).

Milling of Wheat Samples

The clean, tempered wheat samples were milled with a Quadruplex micro mill (17). Three fractions were obtained: flour, shorts, and bran. Owing to the number of small and shrunken kernels in some of the early harvested samples, it was difficult to obtain a perfect separation of all the bran from the flour during the milling process. Ground whole wheat was prepared with a Labconco Mill (Laboratory Construction Co., Kansas City, Mo.).

Protein and Ash

Protein and ash contents of whole wheat, flour, semolina, and bran were determined according to AACC standard procedures (16). Duplicate determinations were performed for each sample and the average value was reported.

Total Reducing and Nonreducing Sugars

Sugars were determined by the alkali ferricyanide procedure (16) with slight modification for the samples collected at the early stages of maturity, which contained high concentrations of sugars. For these samples, a 1-ml. aliquot of the alcohol acid-buffer extract was diluted with 4 ml. of alcohol-acid buffer solution. Thereafter, the regular procedure was followed. Duplicate determinations were performed for each sample and the average value was reported.

Extraction of Free Sugars

Free sugars in flour were extracted, using the ternary solvent system described by Ponte et al. (18). To 1 g. of flour, 2 ml. chloroform and 2 ml. methanol were added. The mixture was then agitated for 20 min. on an automatic shaker. Finally, 2 ml. water was added and the suspension was further mixed for 1 min., and then centrifuged at 7,700 × g for 10 min. The upper layer was decanted and evaporated to a small volume on a flash evaporator (50°C.). The resulting syrup was dissolved in an appropriate volume of 0.1N borate buffer, pH 8, to form the sugar-borate complex.

This system of extracting the free sugars from the flour offers the following advantages, according to Ponte et al. (18): a) the sample is effectively defatted, since the lipids go into the chloroform phase; b) the enzymes are inactivated; and c) the procedure is comparatively rapid and simple.

No detailed investigation was conducted to determine the completeness of extraction with the procedure (18); however, the results obtained between duplicate determinations on the same sample were in good agreement. Also, the extraction procedure used in this study was compared to that of Saunders (4), with very similar results being obtained.

Ion-Exchange Chromatography

The system used to analyze the mono-, di-, and trisaccharides consists of a heavy-wall glass-jacketed glass column, 75 cm. long and 0.6 cm. i.d., the temperature of which was maintained at 45°C. throughout the analysis; a high-pressure micro pump; a proportioning pump; a heating bath, which was maintained at 95°C. for development of the color (15); a colorimeter, to measure absorbance at 420 nm., and a recorder. The column was packed with strongly anionic microspherical exchange resin-Technicon type S chromobeads (technicon Instruments Corp., Tarrytown, N.Y.). Sugar analysis was performed according to

Kessler (15) with minor modifications. The buffer gradient system was that of Catravas (14). The high-pressure micro pump was used to maintain a constant flow-rate of 0.9 ml. per min. throughout the series of experiments. All solutions were deaerated and filtered through Millipore filters (0.45 μ pore size) to remove any possible contaminants.

The identification of the free sugars in the extract was based on the retention time of standard sugars used individually or in combination with other sugars.

Since each sugar reacts differently with the orcinol-reagent (19), a standard curve was established for each sugar. Values reported in this investigation for the free sugars were the result of single determinations.

Following analysis of each sample, which took about 6.5 hr., the column was regenerated for 5 hr. with 5% potassium tetraborate and equilibrated for 1 hr. with 0.1N borate buffer, pH 8.0 (14).

RESULTS AND DISCUSSION

Original Moisture, Test Weight, 1,000-Kernel Weight, and Kernel Size Distribution

During the course of this study, wheat samples were harvested at different stages of maturity with original moisture being used as the criterion of maturity. The investigation was concerned with analytical determinations expressed on a 14.0% moisture basis; however, the stage of maturity was given in terms of days pre-ripe or as percent moisture in the kernel at the time of harvest. The rapid loss of water corresponded to the initiation of the maturation phase. The time of initiation of maturity was not only dependent on the variety, but also on the environmental conditions (9). Tables I and II show the changes in original moisture, test weight,

TABLE I. PRELIMINARY ANALYSIS OF MATURING WHEAT

Days Pre-Ripe	Original Moisture	Test Weight[a] lb./bu.	1,000-Kernel Weight[a] g.	Kernel Size Distribution		
				Large %	Medium %	Small %
		HRS (Justin, 1969)				
21	70.0	30.0	11.9	13.5	73.5	13.0
18	59.9	39.5	16.7	16.0	76.5	7.5
16	58.0	30.5	18.0	29.0	68.0	3.0
13	50.6	43.5	23.6	51.0	48.0	1.0
11	49.3	42.0	28.8	71.0	28.0	1.0
9	43.7	43.5	26.7	59.0	38.0	3.0
4	28.0	50.1	27.2	47.0	50.0	3.0
2	12.5	55.5	33.8	53.5	45.0	1.5
0	9.9	59.0	34.0	54.0	45.0	1.0
		HRS (Justin, 1970)				
29	76.0	22.0	3.1	0	12.0	88.0
23	72.5	29.0	8.0	2.0	44.0	54.0
20	66.9	37.0	14.3	4.5	80.5	15.0
16	58.4	43.0	19.1	13.0	81.5	5.5
13	52.8	44.0	22.2	33.0	64.0	3.0
9	45.0	46.0	25.9	48.5	50.0	1.5
6	43.2	42.0	27.7	70.0	30.0	0
3	31.1	45.0	28.0	55.0	45.0	0
0	17.9	55.0	20.5	48.0	52.0	0

[a]At 14.0% moisture basis.

1,000-kernel weight, and kernel size during the maturation of a variety of HRS (Justin) and durum (Leeds) wheat for the 1969 and 1970 crop years. Original moisture continued to decrease while test weight increased steadily in all varieties with maturation. The percentage of small kernels observed during the early stages of maturity decreased rapidly to a low level. Similar results were reported by Skarsaune (20).

Protein and Ash Contents

A rapid increase in the protein content per kernel was observed early in the maturation of the Justin and Leeds varieties during the 1969 crop year (Table III). This increase continued until the moisture reached about 50%, at which time the protein content leveled off for a period of time and then increased slowly until maturation was complete. These results would indicate that most of the protein accumulation took place during the very early stages of maturity and confirm the work reported earlier by Harris and Mac William (10). It was reported previously (21) that a rapid increase in kernel nitrogen was accompanied by a decrease in leaf and stem nitrogen, indicating translocation from leaves and stem to the kernel.

If the protein content of the samples is expressed on a percentage basis, the protein content of the whole wheat, flour, and semolina increases only very slightly during maturation. The pattern of the changes in total protein during the development of the endosperm resembles the pattern of relative changes in starch and in reducing sugars, and is consistent with a precursor pool-product relationship (9).

The exact changes in the nitrogen metabolism were not investigated; however, it is expected that there would be some changes in the proportions of the constituent protein classes within the wheat kernel during the maturation phase.

TABLE II. PRELIMINARY ANALYSIS OF MATURING WHEAT

Days Pre-Ripe	Original Moisture	Test Weight[a] lb./bu.	1,000-Kernel Weight[a] g.	Kernel Size Distribution Large %	Medium %	Small %
			Durum (Leeds, 1969)			
20	64.0	40.0	17.8	9.0	76.0	15.0
18	61.4	38.5	21.3	20.0	74.0	6.0
15	54.4	40.0	27.0	56.5	42.0	1.5
13	50.3	43.5	31.2	75.0	24.5	0.5
11	44.1	46.3	30.6	59.0	38.5	2.5
6	32.2	55.6	31.7	43.5	53.0	3.5
4	13.8	59.7	34.0	35.5	62.5	2.0
2	10.3	61.0	42.0	61.5	37.0	1.5
0	9.7	63.0	41.0	51.5	47.0	1.5
			Durum (Leeds, 1970)			
...[b]	74.0	20.0	6.3	0	25.0	75.0
...	67.0	36.0	12.9	1.0	34.0	65.0
...	61.4	41.0	19.0	3.0	67.0	30.0
...	51.9	46.0	27.0	30.5	68.0	1.5
...	46.1	46.0	32.0	65.0	34.5	0.5
...	39.9	51.0	35.5	73.0	26.5	0.5

[a]At 14.0% moisture basis. [b]Undetermined due to the environmental conditions.

TABLE III. PROTEIN AND ASH CONTENTS OF MATURING WHEAT, FLOUR, SEMOLINA, AND BRAN

Original Moisture %	Protein[a] Whole-wheat %	Per kernel mg.	Flour %	Bran %	Ash[a] Whole-wheat %	Per kernel mg.	Flour %	Bran %
			HRS (Justin, 1969)					
70.0	12.5	1.49	12.0	12.8	2.05	0.24	1.72	2.67
59.9	12.0	2.00	11.1	12.5	1.87	0.31	1.44	3.03
58.0	12.1	2.18	11.7	12.9	1.84	0.33	1.17	3.28
50.7	12.3	2.90	11.4	13.1	1.78	0.42	0.73	4.27
49.3	12.8	3.69	12.5	14.1	1.69	0.49	0.92	4.82
43.7	12.9	3.44	12.0	15.8	1.66	0.44	0.67	4.95
28.0	13.9	3.78	13.0	16.0	1.79	0.49	0.54	5.50
12.5	13.6	4.60	12.8	15.9	1.90	0.64	0.53	5.47
9.9	13.4	4.56	12.7	15.9	1.79	0.61	0.48	5.58
			Durum (Leeds, 1969)					
64.0	10.8	1.92	10.7	11.1	2.06	0.37	1.66	3.08
61.4	10.6	2.26	10.3	10.9	1.93	0.41	1.44	3.48
54.4	10.6	2.86	10.7	11.2	1.79	0.48	1.13	4.10
50.4	11.3	3.53	10.6	12.2	1.78	0.56	1.14	4.17
44.1	11.4	3.49	11.0	13.1	1.72	0.53	1.00	4.47
32.3	11.4	3.61	10.7	13.7	1.70	0.54	0.92	4.30
13.8	12.0	4.08	11.3	14.7	1.79	0.61	0.92	4.59
10.2	11.5	4.83	10.9	14.4	1.84	0.77	0.95	4.71
9.7	11.7	4.79	10.9	14.1	1.85	0.76	0.99	4.83

[a]At 14.0% moisture basis.

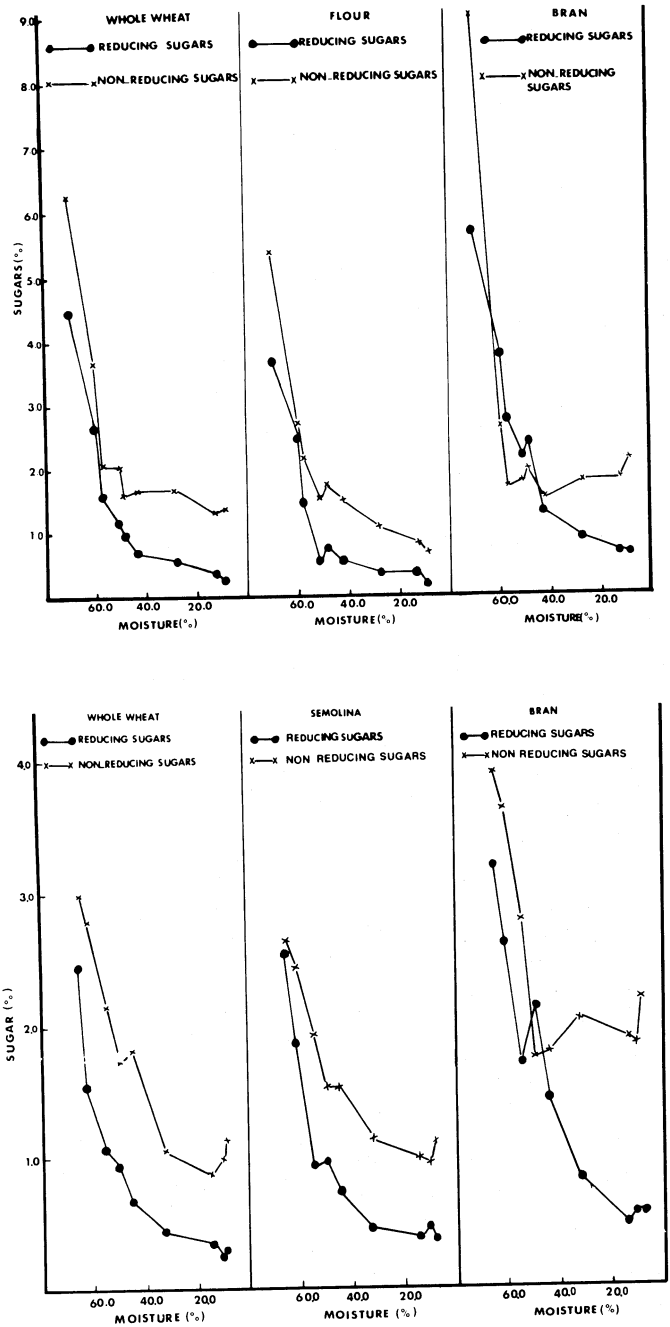
Ash content (Table III), on a per-kernel basis in both varieties, increased uniformly from 0.24 to 0.61 mg. for the HRS wheat variety, and from 0.37 to 0.76 mg. for the durum variety. This increase parallels the increase in the dry-matter deposition. In whole wheat, flour, and semolina, the ash content decreased uniformly during maturation. This tendency toward the decrease in ash content, as the maturation proceeds, could be related to the increased ease of milling as the samples matured (22). In bran, the ash content increased and reached its maximum level by the end of the maturation period.

At approximately the same level of moisture, the durum variety contained in all milled fractions a slightly higher ash content than the HRS wheat variety.

When protein content per kernel was correlated with percent original moisture, correlation coefficients of -0.945** and -0.958** were obtained for the HRS and durum varieties, respectively, for the 1969 crop samples. When ash content per kernel was correlated with percent original moisture, correlation coefficients of -0.959** and -0.926** were obtained for the HRS and the durum varieties, respectively, which coincides with the observation reported earlier (12,20) that the kernel maturation was marked by an increase in protein and ash contents.

Total Reducing and Nonreducing Sugars

Both hard red spring and durum wheats showed a definite decrease in reducing sugars in the whole wheat, flour, semolina, and bran during the maturation period. The maximum levels occurred at the early stages, and the lowest levels at the final stages of maturity (Figs. 1 and 2).



Figs. 1 and 2. Changes in total reducing and nonreducing sugar content during maturation of HRS wheat: top, Justin variety; bottom, Leeds variety. Both at 14.0% moisture basis.

With the nonreducing sugars, a slight decrease was observed with maturation; however, values in the samples approaching maturity were higher than those of the reducing sugars (Figs. 1 and 2).

In the whole wheat, the ratio of reducing and nonreducing sugars in the Justin variety increased from 1:1.4 at the first stage of maturity to 1:9.8 at the final stage of maturity, whereas in the durum variety, Leeds, the ratio increased from 1:1.2 to 1:4.0 at the final stage of maturity. A comparatively similar ratio of reducing to nonreducing sugars had been reported earlier on a durum variety, Langdon, grown under greenhouse conditions (3).

Two other samples – Manitou, a hard red spring wheat, and Lakota, a durum wheat grown during the same crop year – showed a similar trend.

On a per-kernel basis (Table IV), the reducing sugars in the HRS variety (Justin) ranged from 0.53 mg. at 70% original moisture to 0.05 mg. in the mature kernel. In the durum variety, Leeds, the range on a kernel basis varied from 0.43 mg. at 64% moisture to 0.12 mg. in the mature kernel.

When the nonreducing sugars content was expressed on a per-kernel basis (Table IV), fluctuation in the values was observed at the different stages of maturity. In the HRS variety (Justin), values ranged from 0.74 mg. at 70% original moisture to 0.21 mg. in the mature grain. In the durum variety (Leeds), the range varied from 0.53 mg. at 64% moisture to 0.46 mg. in the mature grain. This, however, does not agree with the observations reported by Jennings and Morton (9), that the nonreducing sugars per kernel remained relatively uniform during development.

TABLE IV. TOTAL REDUCING AND NONREDUCING SUGARS IN MATURING WHEAT KERNEL

Original Moisture %	Reducing Sugars[a,b] mg./kernel	Nonreducing Sugars[a,c] mg./kernel
	HRS (Justin, 1969)	
70.0	0.53	0.74
59.9	0.46	0.60
58.0	0.29	0.37
50.7	0.28	0.48
49.3	0.29	0.45
43.7	0.18	0.20
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
61.4	0.33	0.60
54.4	0.29	0.58
50.4	0.29	0.54
44.1	0.21	0.56
32.2	0.14	0.33
13.8	0.12	0.30
10.3	0.10	0.42
9.7	0.12	0.46

[a]At 14.0% moisture basis. [b]Expressed as maltose. [c]Expressed as sucrose.

Correlation coefficients of -0.919** and -0.903** between 1,000-kernel weight and reducing sugars were obtained for the HRS and the durum varieties, respectively. Likewise, when 1,000-kernel weight was correlated with reducing sugars in wheat flour or semolina, correlation coefficients of -0.899** and -0.884** were obtained. Similar significant correlation coefficients were obtained between 1,000-kernel weight and nonreducing sugars. These significant correlations suggest that both the reducing and nonreducing sugars are significantly related to the increase in the maturity of the kernel.

When percent reducing and nonreducing sugars in wheat flour or semolina were correlated with percent starch (unpublished work) in flour or semolina, highly significant correlation coefficients were obtained. The same was true when 1,000-kernel weight was correlated with starch percent in flour or semolina. This suggests that starch synthesis depletes the pool of precursor compounds during the maturation process as suggested by Jennings and Morton (9). Also, it has been reported that although active starch synthesis starts early after flowering, it continues to be synthesized during the maturation stages (9,12).

Free Sugars: General Note

The group of sugars studied in this investigation were the mono-, di-, and trisaccharides which are present in the aqueous methanol layer of the ternary system described by Ponte et al. (18), and would include raffinose, sucrose, maltose, glucose, and fructose.

Other sugars, present in the same extract, were observed during the chromatographic analysis. These sugars appeared as two distinct peaks on the chromatogram and were the first to be eluted from the column. They showed a progressive decrease during maturation. Preliminary tests indicated that this group was composed of fructose and glucose and probably are glucofructans. Future work will be directed at the investigation of these two sugar components.

Free Sugars: HRS Wheat Flour

Figure 3 shows graphically the change in content for each of the five sugars – fructose, glucose, sucrose, maltose, and raffinose – present in Justin flour at the different stages of maturity for the 1969 crop year. In the early stages, fructose, glucose, and sucrose were the principal predominant simple sugars in the flour extract.

Fructose. Fructose declined sharply from 1.05 to 0.11% as the original moisture decreased from 70 (Stage 1) to 49.3% (Stage 5) (Fig. 3), then reached its minimum concentration, 0.02%, at the final stage of maturity. In the 1970 crop year (Table V), however, a sharp decrease in fructose concentration occurred as the original moisture decreased from 76.0 to 52.8%. Fructose reached the lowest concentration of 0.01% when the original moisture reached 17.9%. This would indicate that utilization of fructose in the endosperm of Justin wheat occurred during the early stages of maturity.

Glucose. Glucose followed a pattern similar to that of fructose; however, the change was gradual rather than abrupt. The concentration of glucose dropped from 0.71% at 70% original moisture (Stage 1) to 0.07% when the kernel reached maturity (Fig. 3). In the Justin flour of the 1970 crop (Table V) a similar trend was observed.

Sucrose. During both crop years, sucrose showed a fluctuating trend (Fig. 3,

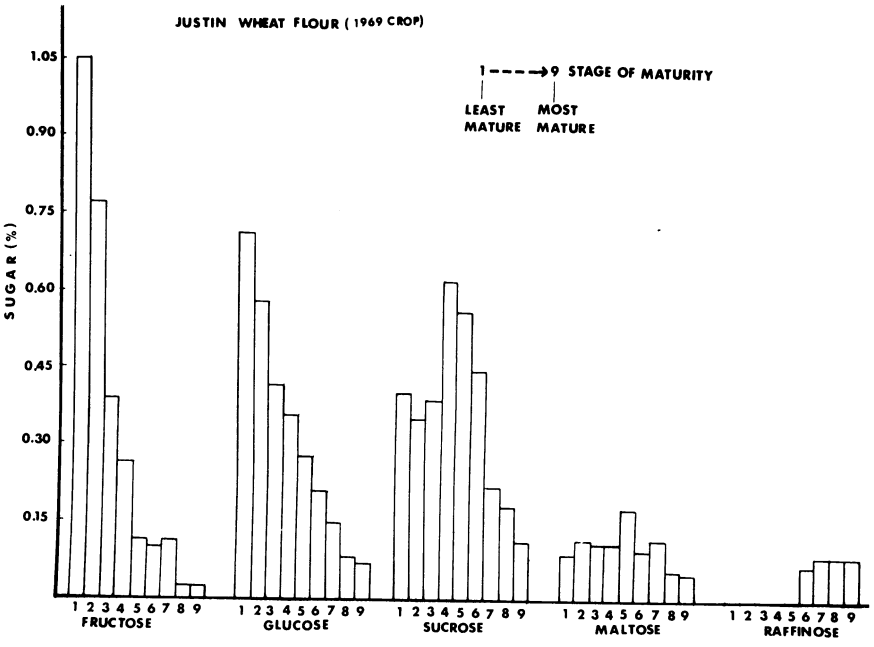


Fig. 3. Change in free sugars during maturation of HRS wheat, (Justin variety, at 14.0% moisture basis).

TABLE V. FREE SUGARS IN MATURING WHEAT[a]

Original Moisture %	Sucrose %	Raffinose %	Maltose %	Fructose %	Glucose %
		HRS (Justin, 1970)			
76.0	0.65	0.00	0.20	3.10	1.54
72.5	0.34	0.00	0.17	1.87	1.00
66.9	0.36	0.00	0.18	0.90	0.75
58.4	0.31	0.08	0.33	0.33	0.18
52.8	0.36	Trace	0.10	0.11	0.18
45.0	0.35	Trace	0.10	0.07	0.14
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
67.0	0.48	0.00	0.12	0.81	0.65
61.4	0.31	0.00	0.10	0.10	0.31
51.9	0.42	0.00	0.11	0.12	0.22
46.1	0.34	0.09	0.08	0.08	0.12
39.9	0.41	0.19	0.07	0.07	0.10

[a]At 14.0% moisture basis.

Table V). In the 1969 crop, sucrose concentration increased from 0.40 to 0.62% as the original moisture decreased from 70.0 (Stage 1) to 50.7% (Stage 4), followed by a relatively gradual decrease until the end of the maturation period. In the 1970 crop (Table 5), sucrose concentration dropped from 0.65 to 0.32% when the original moisture decreased from 76 to 43.2%. As the wheat reached maturity, the concentration decreased to 0.08%.

Maltose. Maltose in the 1969 crop year (Fig. 3) reached its highest level, 0.18%, at 49.3% original moisture (Stage 5), and then dropped to 0.05% at the final stage of maturity. A similar trend was observed in the 1970 crop (Table V): the concentration increased from 0.20 to 0.33% as the original moisture decreased from 76.0 to 58.4%. The amount of maltose then decreased to its lowest level, 0.03%, at the final stage 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 (23).

Raffinose. Raffinose was not present in the flour during the early stages of maturity. In Justin wheat flour of the 1969 crop (Fig. 3), raffinose appeared at a low concentration, 0.07%, when the original moisture reached 43.7% (Stage 6), and increased slightly during the final stages of maturity. In the 1970 crop (Table V), raffinose was detected at an earlier stage. However, there was greater fluctuation for the remaining stages than was observed in the 1969 crop samples.

The results of this work agree with the findings of Matsushita (8) and of Harris and MacWilliam (10), who reported that raffinose appears only in the later stages during ripening of wheat and naked barley; however, this does not agree with observations of Menger (3), who reported that raffinose was present in high concentrations during all stages of maturity. Harris and MacWilliam (10) suggested that raffinose possibly has some special metabolic significance.

Free Sugars: Durum Wheat Semolina

Changes in the free sugars during the maturation of durum Leeds semolina for the 1969 crop year are shown graphically in Fig. 4, and in tabular form for the 1970 crop year (Table V). The changes in the free sugars in durum wheat showed a similar trend to the changes observed previously in Justin wheat flour, with the exception of sucrose and raffinose.

Sucrose

Sucrose (Fig. 4) reached its maximum concentration when the moisture reached 54.4% (Stage 3). This was followed by values which fluctuated somewhat toward the end of the maturation period. The differences in concentration of sucrose in the semolina from the fully mature Leeds wheat and in the flour from the mature Justin wheat in the 1969 crop was 0.15% at approximately the same moisture content.

Raffinose

Raffinose was present in larger amounts in durum-wheat semolina than in HRS wheat flour. In the 1969 crop year (Fig. 4) it appeared at a high concentration, 0.21%, when the original moisture decreased to 32.3% (Stage 6) and then decreased to 0.17% at the final stage of maturity. However, in the 1970 crop (Table V), raffinose was detected at an earlier stage when the original moisture reached 46.1%.

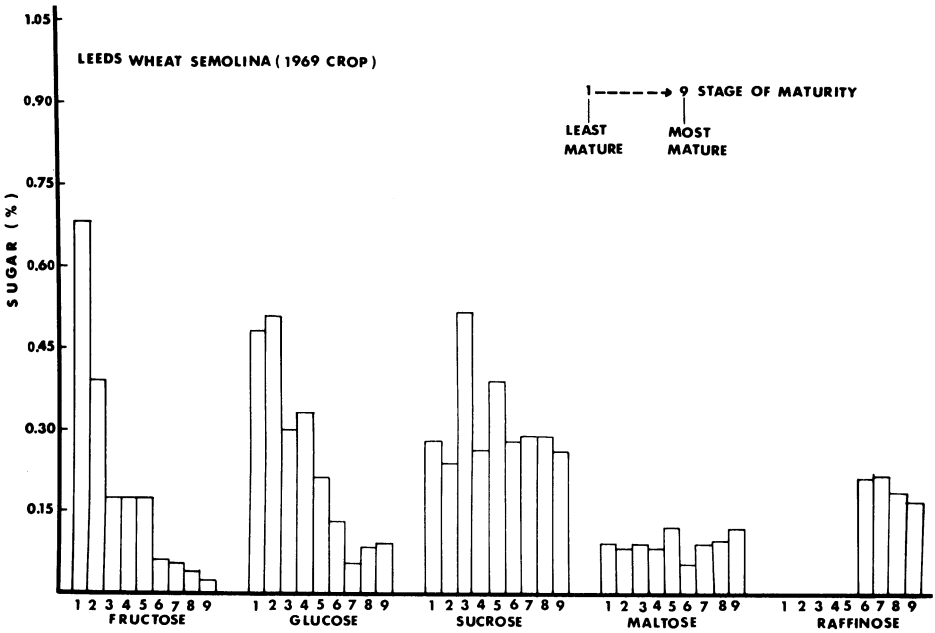


Fig. 4. Change in free sugars during maturation of durum wheat (Leeds variety, at 14.0% moisture basis).

Unfortunately, due to the loss of samples during the 1970 crop year, the remaining results could not be ascertained.

The differences between and among varieties in regard to their free-sugar content may be explained by the fact that the period from flowering to full maturity is relatively constant for a given variety in a given environment, but varies greatly when all varieties and environments are considered, the environmental factors being responsible for the greater variation (10,24).

In conclusion, it can be seen that the changes in fructose, glucose, sucrose, and raffinose parallel the changes in the reducing and nonreducing sugars, which in turn parallel the changes in the moisture content of the endosperm during the stages of maturity. These relationships are consistent with the rate of starch synthesis. As suggested earlier by Wood (25), sucrose, which is translocated to the whole grain, is a precursor of part of the starch. Glucose-1-phosphate is formed by the phosphorolysis of sucrose in the endosperm. The glucose-1-phosphate is then converted to uridine diphosphate glucose, which is involved in amylose synthesis by glucosyl transfer.

Literature Cited

1. HARRIS, G., and MacWILLIAM, I. C. Carbohydrates in malting and brewing. II. Changes in the carbohydrates of barley during ripening, drying, and storage. J. Inst. Brew. (London) 60: 387 (1954).
2. FRASER, J. R., and HOLMES, D. C. Proximate analysis of wheat flour carbohydrates. IV. Analysis of whole meal flour and some of its fractions. J. Sci. Food Agr. 10: 506 (1959).
3. MENGER, A. Untersuchungen über di Möglichkeit einer beziehung zwischen den löslichen kohlenhydraten in durum weizen und nichtenzymatischen bräunungerscheinungen. Ber. Getreidechem. Tag. 7: 101 (1961).

4. SAUNDERS, R. M., and WALKER, H. G., Jr. The sugars of wheat bran. Cereal Chem. 46: 85 (1969).
5. BAILEY, C. H. The chemistry of wheat and wheat products, p. 37. Chemical Catalog Co.: New York (1925).
6. McCALLA, A. G., and NEWTON, R. Effect of frost on wheat at progressive stages of maturity. II. Composition and biochemical properties of grain and flour. Can. J. Res. 13: 1 (1935).
7. MILLER, E. C. A physiological study of the winter wheat plant at different stages of its development. Kans. State College Tech. Bull. 47 (1939).
8. MATSUSHITA, A. Changes of the free sugar content in seeds of cereals during ripening. Free sugar contents in seed of wheat and naked barley. Eiyo To Shokuryo 22: 371 (1969).
9. JENNINGS, A. C., and MORTON, R. K. Changes in carbohydrates, protein, and non-protein nitrogenous compounds of developing wheat grain. Aust. J. Biol. Sci. 16: 318 (1963).
10. HARRIS, G., and MacWILLIAM, I. C. VI. Changes in the carbohydrate composition of barley on ripening and corresponding variations in nitrogenous constituents. J. Inst. Brew. (London) 63: 210 (1957).
11. MERRITT, N. R., and WALKER, J. T. Development of starch and other components in normal and high amylose barley. J. Inst. Brew. (London) 75: 156 (1969).
12. MacGREGOR, A. W., LaBERGE, D. E., and MEREDITH, W.O.S. Changes in barley kernels during growth and maturation. Cereal Chem. 48: 255 (1971).
13. KHYM, J. X., and ZILL, L. P. The separation of sugars by ion exchange. J. Amer. Chem. Soc. 74: 2090 (1952).
14. CATRAVAS, G. N. New developments in automatic sugar chromatography. In: Automation in analytical chemistry, p. 397. Mediad: New York (1967).
15. KESSLER, R. B. Rapid quantitative anion-exchange chromatography of carbohydrates. Anal. Chem. 39: 1416 (1967).
16. AMERICAN ASSOCIATION OF CEREAL CHEMISTS. AACC Approved methods, 7th ed. The Association: St. Paul, Minn. (1962).
17. SHUEY, W. C. Measuring the commercial milling value of plant breeders wheat samples. The A.O.M. Bulletin, p. 2884 (1965).
18. PONTE, J. G., Jr., DeSTEFANIS, V. A., and TITCOMB, S. T. Application of thin-layer chromatography to sugar analysis in cereal based products. (Abstr.) Cereal Sci. Today 14(3): No. 100 (1969).
19. DISCHE, Z. Color reactions of pentoses. In: Methods in carbohydrate chemistry, p. 285, R. L. Whistler and M. L. Wolfrom, eds.; Vol. I. Academic Press: New York (1962).
20. SKARSAUNE, S. K., YOUNGS, V. L., and GILLES, K. A. Changes in wheat lipids during seed maturation. I. Physical and chemical changes in the kernel. Cereal Chem. 47: 522 (1970).
21. McNEAL, F. H., BERG, M. A., and WATSON, C. A. Nitrogen and dry matter in five spring wheat varieties at successive stages of development. Agron. J. 58: 605 (1966).
22. HARRIS, R. H., HELGESON, E. A., and SIBBITT, L. D. The effect of maturity upon the quality of hard red spring and durum wheats. Cereal Chem. 20: 447 (1943).
23. GREECH, R. G. Carbohydrate synthesis in maize. Advanc. Agron. 20: 275 (1968).
24. PETERSON, R. F. In: Wheat, p. 44. Interscience Publishers, Inc.: New York (1965).
25. WOOD, H. L. A study of some carbohydrate relationships in the wheat plant and of wheat starch extracted from mottled and unmottled grain. Aust. J. Agr. Res. 11: 673 (1960).

[Received November 2, 1971. Accepted April 28, 1972]