1 h at 95 °C. Treatment of this reaction mixture with diazomethane gave a number of products with the two most intense spots (after exposure to iodine) corresponding to materials g and f in the benzene–ethyl acetate solvent system (Figure 3B).

Although material f has essentially the same R_f value as dimethyl benzylpenicilloate, TLC analysis of the chloroform reaction mixture before treatment with diazomethane indicated absence of large quantities of benzylpenicilloic acid. Isolation of material f by preparative TLC gave a material whose mass spectrum was essentially identical with V, indicating that material no. 6 is either an isomer or mixture of isomers of IV.

ACKNOWLEDGMENT

The authors are grateful to John W. Turczan, FDA New York District Laboratories for the NMR spectrum of V and to Kurt L. Loening, Chemical Abstracts Service, for naming IV and V.

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Received for review January 18, 1977. Accepted April 27, 1977. Paper of the Journal Series, New Jersey Agricultural Experiment Station, New Brunswick, N.J. This work was supported by funds from Food and Drug Administration Contract FD-179 and the Charles and Johanna Busch Memorial Fund. Presented in part, Division of Agricultural and Food Chemistry, 172nd National Meeting of the American Chemical Society, San Francisco, August, 1976.

Saccharides of Maturing Triticale, Wheat, and Rye

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The saccharide content of two tall triticales, two semidwarf "Armadillo" triticales, one spring wheat, one rye, and two durum wheats was determined in kernels of different maturity. Monosaccharides, which were present in grain kernels 4 weeks before maturity, were no longer detectable 2 weeks before the final harvest. Maltose and maltotriose were present in low and unchanging amounts. Sucrose, raffinose, and kestose increased as the grains matured, while the tetrasaccharides decreased. Although the saccharide composition of the kernels from the different cereal grains differed, the trends in triticales were similar to those of the parental species, wheat and rye, during maturation.

Changes in chemical composition of maturing wheat have been studied. The rate of grain filling is similar for wheat, barley, oats, and rye, suggesting a common physiological process (Meredith and Jenkins, 1976b). The decline in percentage moisture observed during the development of cereal grains is due to gain in dry matter (Meredith and Jenkins, 1975), although the yield of dry matter varies considerably (Meredith and Jenkins, 1970).

Changes in carbohydrates, protein and nonprotein nitrogen compounds of maturing wheat have been reported (Jennings and Morton, 1963). Several carbohydrates and their hydrolyzing enzymes were determined (Meredith and Jenkins, 1973a,b, 1975, 1976a,b).

Changes in maturing triticale do not appear to parallel in entirety those changes in other cereal grains (Lorenz and Welsh, 1976). Triticale kernels, which are plump and relatively large in size compared to wheat up to about 3 weeks before maturity, shrivel during the late stages of kernel development, and α-amylase activity tends to be high (Klassen and Hill, 1971; Lorenz and Welsh, 1976).

This study follows the changes in saccharide content during triticale kernel development and compares these changes to those in the maturing parental species, wheat and rye.

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MATERIALS AND METHODS

a. Sample Identification and Preparation. Two tall spring triticales (6-TA-204 and 6-TA-206), two semidwarf "Armadillo" triticales (RF720009 and RF720011), a hard red spring wheat (Colano), two spring semidwarf durums (RF710066 and 710222), and Prolific spring rye were studied. Plots at the Colorado State University Agronomy Research Center, Fort Collins, were seeded April 10, 1974 and several rows of each cultivar harvested July 8, 22, 29 and August 6 and 12. Moisture contents of the samples at harvest are given in Table I.

Except for the samples harvested July 8, 20 g of each grain sample were frozen approximately 2 h after harvest. All samples were placed in a freeze dryer the following morning. The July 8 samples of necessity were hand harvested which delayed freezing until 8 h after harvest.

Table I. Moisture Content of Samples at Harvest

Sample	Moisture content, %					
	July 8	July 15	July 22	July 29	Aug 6	Aug 12
Colano spring wheat	47.8	44.2	27.2	13.1	12.9	
Durum wheat RF 710066	64.0	41.1	36.6	16.9	11.8	
Durum wheat RF 710222	51.3	43.1	37.4	12.8	10.9	
Profilic spring rye	67.0	56.7	45.7	35.9	27.0	20.8
Triticale 6-TA-204	60.0	55.1	49.6	34.2	15.1	12.0
Triticale 6-TA-206	65.2	63.8	51.5	36.8	34.7	18.6
Armadillo triticale RF 720009	58.2	48.3	38.2	19.1	13.3	
Armadillo triticale RF 720011	58.8	54.6	35.9	20.2	13.3	

All other samples were threshed. The lyophilized samples were stored at room temperature in taped screw cap bottles until assayed for sugars.

Sugar determinations were carried out as follows. The lyophilized grain kernels were milled 20–30 s in a stainless steel ball mill. Weighed amounts of the powder were mixed with 70% ethanol (v/v) in a screw cap vial to give 100 mg/mL, heated at 80–85 °C for 1 h, cooled, and centrifuged. Aliquots of the supernatant were evaporated to dryness under nitrogen and silylated overnight at room temperature with Tri-Sil reagent (Becker et al., 1974). All grain samples were analyzed at least twice.

b. Gas-Liquid Chromatographic (GLC) Separation and Quantitation. The saccharides were separated on a Hewlett Packard 5830 gas chromatograph with flame ionization detectors. The unit was equipped with dual $^1/_8$ in. × 3 ft stainless steel columns packed with 3% OV-1 on Chromosorb W (HP80-100). It was temperature programed for a 5 °C/min temperature rise from 200 °C for 9 min and then a 20 °C temperature rise to 330 °C where it was held for 8 min. The injector and detector were at 330 °C. Sucrose and maltose were identified by comparison of retention times with standards run under the same conditions. The trisaccharides raffinose and kestose have identical elution times and were thus quantified using known amounts of raffinose. The tetrasaccharides nystose and fructosylraffinose also coelute, and these were quantified using known amounts of the similar tetrasaccharide stachyose. This assay does not detect variations in the ratio of raffinose to kestose nor nystose to fructosylraffinose. The monosaccharides glucose, fructose, and galactose were eluted from the column before sucrose; these were not quantified. They were not present in the grains after the July 22nd harvest date.

RESULTS AND DISCUSSION

Monosaccharides were present in detectable amounts 4 weeks before full maturity in all but the Colano and durum wheat samples. However, during later development stages, they were no longer detectable (Table II). In the Colano and durum wheat, only grains of the first harvest (July 8) contained monosaccharides. This disappearance of monosaccharides is consistent with observations on wheat grains by Meredith and Jenkins (1973a, b).

The presence of maltose and malotriose in low, generally unchanging amounts (Table II) is somewhat surprising. It could possibly be due to high levels of maltase. High maltase activity has not been reported, however, in these grains. A rather high α-amylase activity has been found in these same samples, particularly near and at full maturity (Lorenz and Welsh, 1976). High α-amylase activity in triticales has also been reported by others (Müntzing, 1963; Klassen and Hill, 1971; Berry et al., 1971). It appears, therefore, that any breakdown of starch due to high α-amylase activity, as has been postulated to occur and as being responsible for kernel shriveling (Lorenz, 1974) does not proceed to the maltose or maltotriose level. These results cast doubts upon the validity of unduly large starch degradation by α-amylase as being the cause of kernel shriveling observable in all triticales.

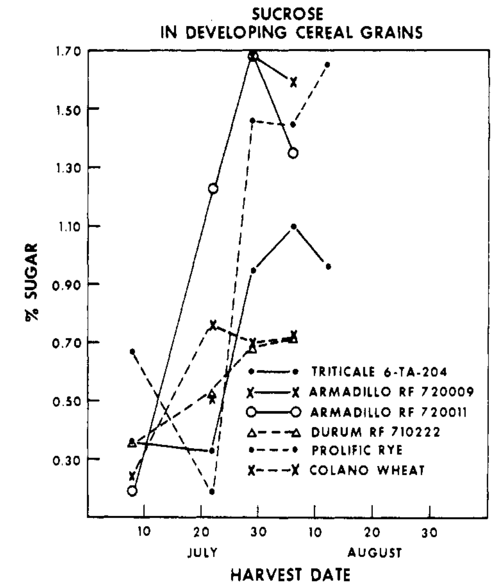

Figure 1. Sucrose in developing cereal grains.

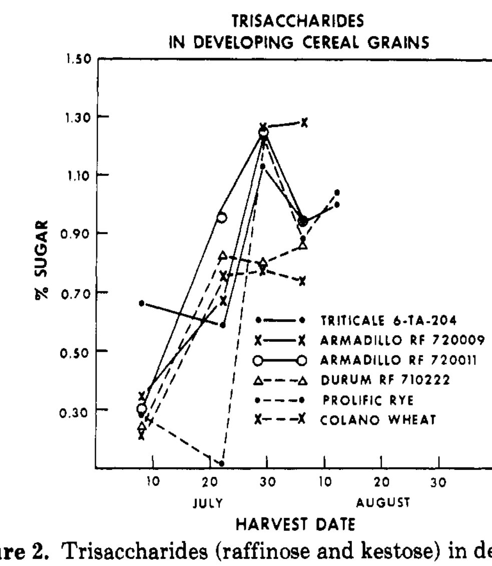

Figure 2. Trisaccharides (raffinose and kestose) in developing cereal grains.

The content of sucrose increased two–three-fold in the tall triticales (6-TA-204 and 6-TA-206), Colano spring wheat, Prolific spring rye, and the durum wheat RF720222, whereas a seven–eight-fold increase occurred in the semidwarf triticales (RF720009 and RF720011) and durum wheat RF710066, in mature kernels compared to earlier development stages (Figure 1).

The content of raffinose and kestose increased less than onefold in the tall spring triticales, but from three- to

Table II. Monosaccharides, Maltose, and Maltotriose in Developing Cereal Grains[a]

Harvest date	Percent sugar, dwb					
	Mono-saccharides	Maltose	Maltotriose	Mono-saccharides	Maltose	Maltotriose
	Triticale 6-TA-204			Triticale 6-TA-206		
8 July	+	0	0	+	0	0
22 July	+	0	0	+	0.07 ± 0.02	0
29 July	–	0	0	–	0.04 ± 0.01	0
6 Aug	–	0	0	–	0.06 ± 0.01	0.04 ± 0.00
12 Aug	–	0	0	–	0.04 ± 0.01	0
	Armadillo Triticale RF 720009			Armadillo Triticale RF 720011		
8 July	+	0.04 ± 0.01	0.01 ± 0.01	+	0.09 ± 0.01	0.01 ± 0.01
22 July	+	0.07 ± 0.02	0.04 ± 0.01	+	0.10 ± 0.01	0.06 ± 0.02
29 July	–	0.11 ± 0.03	0.11 ± 0.02	–	0.12 ± 0.02	0.09 ± 0.04
6 Aug	–	0.06 ± 0.02	0	–	0.08 ± 0.02	0.06 ± 0.01
	Colano Spring Wheat			Prolific Spring Rye		
8 July	+	0.04 ± 0.01	0.01 ± 0.00	+	0.00	0.02 ± 0.01
22 July	–	0.03 ± 0.00	0	+	0.03 ± 0.01	0.01 ± 0.01
29 July	–	0.04 ± 0.00	0	–	0.04 ± 0.01	0.03 ± 0.01
6 Aug	–	0.04 ± 0.00	0	–	0.04 ± 0.02	0.02 ± 0.02
12 Aug	–			–	0.03 ± 0.01	0.01 ± 0.01
	Durum Wheat RF 710066			Durum Wheat RF 710222		
8 July	+	0.12 ± 0.02	0	+	0.09 ± 0.01	0
22 July	+	0.04 ± 0.01	0	–	0.10 ± 0.01	0
29 July	–	0.11 ± 0.01	0	–	0.13 ± 0.04	0
6 Aug	–	0.11 ± 0.01	0	–	0.13 ± 0.04	0

[a] Averages and standard deviations.

Table III. Saccharides per Kernel in Developing Cereal Grains[a]

Harvest date	Percent sugar					
	Sucrose	Trisaccharides	Tetrasaccharides	Sucrose	Trisaccharides	Tetrasaccharides
	Triticale 6-TA-204			Triticale 6-TA-206		
8 July	0.14 ± 0.01	0.26 ± 0.04	0.46 ± 0.06	0.20 ± 0.06	0.27 ± 0.03	0.55 ± 0.04
22 July	0.17 ± 0.00	0.30 ± 0.04	0.23 ± 0.01	0.06 ± 0.01	0.10 ± 0.03	0.02 ± 0.01
29 July	0.62 ± 0.04	0.74 ± 0.05	0.25 ± 0.05	0.72 ± 0.13	0.58 ± 0.11	0.13 ± 0.04
6 Aug	0.93 ± 0.09	0.80 ± 0.11	0.29 ± 0.17	0.82 ± 0.22	0.57 ± 0.04	0.09 ± 0.01
12 Aug	0.84 ± 0.06	0.88 ± 0.09	0.23 ± 0.04	0.82 ± 0.13	0.58 ± 0.05	0.07 ± 0.06
	Armadillo Triticale RF 720009			Armadillo Triticale RF 720011		
8 July	0.10 ± 0.03	0.14 ± 0.03	0.27 ± 0.10	0.08 ± 0.00	0.12 ± 0.10	0.17 ± 0.04
22 July	0.31 ± 0.08	0.41 ± 0.01	0.35 ± 0.07	0.79 ± 0.09	0.61 ± 0.01	0.26 ± 0.01
29 July	1.36 ± 0.31	1.02 ± 0.03	0.50 ± 0.14	1.34 ± 0.22	1.00 ± 0.05	0.24 ± 0.01
6 Aug	1.38 ± 0.13	1.11 ± 0.14	0.44 ± 0.17	1.17 ± 0.33	0.80 ± 0.22	0.14 ± 0.10
	Colano Spring Wheat			Prolific Spring Rye		
8 July	0.13 ± 0.01	0.11 ± 0.02	0.11 ± 0.03	0.22 ± 0.01	0.10 ± 0.00	0.43 ± 0.03
22 July	0.55 ± 0.09	0.55 ± 0.04	0.01 ± 0.01	0.10 ± 0.02	0.06 ± 0.01	0.03 ± 0.01
29 July	0.61 ± 0.05	0.67 ± 0.04	0.01 ± 0.01	0.94 ± 0.07	0.79 ± 0.04	0.30 ± 0.02
6 Aug	0.63 ± 0.10	0.64 ± 0.10	0.01 ± 0.01	0.93 ± 0.13	0.56 ± 0.02	0.17 ± 0.02
12 Aug				1.31 ± 0.06	0.82 ± 0.01	0.31 ± 0.06
	Durum Wheat RF 710066			Durum Wheat RF 710222		
8 July	0.04 ± 0.00	0.03 ± 0.00	0	0.17 ± 0.01	0.12 ± 0.00	0.03 ± 0.00
22 July		0.01 ± 0.01	0	0.32 ± 0.01	0.52 ± 0.01	0.01 ± 0.01
29 July	0.66 ± 0.04	0.73 ± 0.01	0.08 ± 0.01	0.59 ± 0.03	0.70 ± 0.08	0.01 ± 0.00
6 Aug	0.74 ± 0.06	0.83 ± 0.04	0.10 ± 0.01	0.64 ± 0.01	0.77 ± 0.02	0.01 ± 0.01

[a] Averages and standard deviations.

fourfold in almost all other samples during the development process (Figure 2). One exception was observed in durum wheat RF710066; here trisaccharide content increased about 12-fold during the last 4 weeks before final harvest.

The tetrasaccharide level remained essentially unchanged in the semidwarf triticale RF720009 and the two durum wheat samples. It decreased from two- to tenfold in all other samples, as illustrated in Figure 3. This trend is consistent with changes in tetrasaccharide levels in wheat during kernel development reported by Meredith and Jenkins (1973a, b).

While the cereal chemist and the food technologist may prefer to look at compositional data expressed on a 14% moisture basis or on a dry weight basis (Table II and Figures 1–3), the plant breeder and geneticist may prefer to see such data expressed on a per kernel basis which, because of the constantly changing moisture levels of these kernels during development, show different trends in some instances. Generally, increases in sucrose and trisaccharides, and decreases in tetrasaccharide levels, are still apparent, when sugar contents are expressed on a per kernel basis (Table III). Levels of maltose and maltotriose which were relatively unchanged during kernel development, when results are expressed on a dry basis, show a gradual increase, when values are expressed on a per kernel basis.

CONCLUSIONS

Changes in saccharide composition of maturing triticales were similar to those in maturing wheat and rye. Sucrose and trisaccharides increased, while the tetrasaccharides decreased, although the amounts found in kernels from the different cereal grain varieties differed. Maltose and

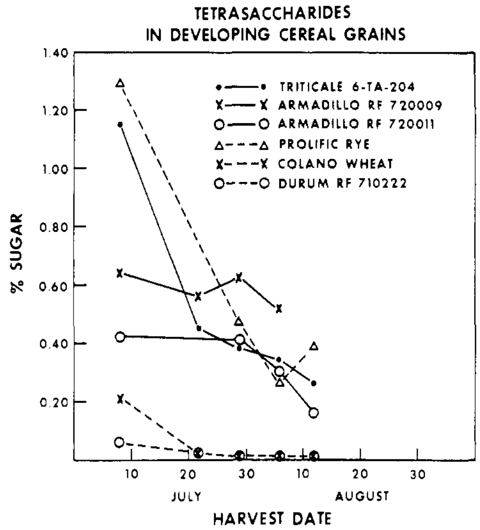

Figure 3. Tetrasaccharides (nystose and fructosylraffinose) in developing cereal grains.

maltotriose were present in triticales in very small amounts only, which was unexpected because of the reported high α-amylase activity in these grains. It is postulated that any starch degradation due to α-amylase activity is minimal. It is unlikely that kernel shriveling in triticale is a result of α-amylase degradation of starch.

ACKNOWLEDGMENT

The authors thank J. Welsh, Department of Agronomy, Colorado State University, Fort Collins, Colorado, for supplying the samples.

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Received for review February 22, 1977. Accepted May 24, 1977.
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Differences in Concentrations and Interrelationships of Phytate, Phosphorus, Magnesium, Calcium, Zinc, and Iron in Wheat Varieties Grown under Dryland and Irrigated Conditions

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Differences in concentrations and interrelationships of total P (TP), phytate P (PP), nonphytate P (NP), PP as percent of TP, Mg, Ca, Zn, and Fe, together with yield, in grains of eight Iranian ("Derakhshan, Harbash, Jawanjani, Jolgeh, Kalheidari, Koohrang, Ommid, and Roshan") and two foreign ("Penjamo and Tobari") varieties of wheat (*Triticum aestivum* L.) grown under dryland and irrigated conditions were determined. Highly significant differences were obtained among varieties and between the two irrigation treatments for most of the variables under study. When wheat varieties were grown under dryland conditions, the grain yield and the concentrations of TP and PP were significantly reduced while those of NP, Ca, and Mg were increased as compared with when grown under irrigation. Concentrations of the grain Zn and Fe did not seem to be affected by irrigation treatment. The four P variables (TP, PP, NP, and PP as percent of TP) were found to be highly correlated under both dryland and irrigated conditions. A high-yielding variety with low phytate and high mineral contents was suggested as ideal to be grown in either dryland or irrigated farming areas.

Phytate P is shown to constitute 49 to 80% of the total P in wheat grain (Knowles and Watkins, 1932; Booth et al., 1941; Asada et al., 1968; Nelson et al., 1968; O'Dell et al., 1972; Abernethy et al., 1973; Nahapetian and Bassiri, 1975, 1976). Phytic acid is present as a mixed insoluble salt of Mg, Ca, and K (Averill and King, 1926) and gradually releases the stored P during germination of the grain (Hall and Hodges, 1966; Asada et al., 1968; Williams, 1970).

There are numerous studies which show that phytic acid reduces the physiological availability of dietary Mg (McCance and Widdowson, 1942; Roberts and Yudkin, 1960; Likuski and Forbes, 1965), Ca (Harrison and Mellanby, 1939; McCance and Widdowson, 1942; Krebs and Mellanby, 1943; Hoff-Jorgensen et al., 1946; Cullumbine et al., 1950; Nelson et al., 1968; Berlyne et al., 1973; Reinhold et al., 1973b), Zn (O'Dell and Savage, 1960; Prasad et al., 1963; O'Dell, 1969; Reinhold, 1971, 1975a,b;

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