Effect of Spaghetti Processing on Semolina Carbohydrates¹

C. LINTAS² and B. L. D'APPOLONIA³, North Dakota State University, Fargo 58102

ABSTRACT

An investigation was conducted to determine the changes which occur in the carbohydrate constituents as a result of processing of semolina into spaghetti. Starch, water-soluble, and water-insoluble pentosans were isolated from semolina and the spaghetti processed from it. The pasting properties, water-binding capacity, and starch damage value of the isolated starches were all affected by processing. Samples taken at different stages during processing showed that some damage of starch took place during mixing and extruding, but particularly during drying. Measurement of the free sugars at different stages during processing revealed considerable differences in the amounts of glucose and maltose present in semolina and spaghetti. These data are in agreement with the changes in starch damage. Water-soluble pentosans were purified by α-amylase treatment to remove soluble starch. The purified pentosans were fractionated on a DEAE-cellulose column into five fractions followed by analysis of each fraction. The ratio of component sugars indicated differences in the amounts of galactose and arabinose present as a result of processing. Water-insoluble pentosans were similarly purified with α -amylase, fractionated on DEAE-cellulose, and analyzed.

The changes in the carbohydrate constituents of bread wheat following breadmaking have been studied by several workers (1). However, at the present time, little or no information is available in the literature concerning the effect of pasta processing on the carbohydrate constituents of durum wheat.

Consequently, a study to investigate the changes, if any, affecting the carbohydrate fraction of durum wheat following pasta processing was undertaken.

MATERIALS AND METHODS

Semolina Samples

The wheat varieties used (Leeds, Mindum, and Hercules) were field plot samples grown in North Dakota during the 1969-70 crop years and milled on a Buhler mill. In addition, two pure cultivars of durum wheat (Leeds and Yuma) grown in North Dakota and artificially sprouted in the field according to the method developed by Dick (2) were used.

Spaghetti Samples

Spaghetti was processed on a semicommercial pasta extruder (DeMaco) according to the procedure used by the Department of Cereal Chemistry and Technology (3), under the following conditions:

Temperature	49.5° C.
Extruding Rate	20 r.p.m.
Absorption	31%
Vacuum	18 in. Hg

¹ Presented at the 57th Annual Meeting, Miami Beach, Oct. Nov. 1972. Published with the approval of the Director of the Agricultural Experiment Station, North Dakota State University, Fargo, as Journal Series No. 408. Taken in part from a thesis to be submitted by Claudia Lintas to North Dakota State University, in partial fulfillment of the requirements for the Ph.D. degree.

2Present address: Istituto Nazionale Della Nutrizione, Rome, Italy.

University.

³Assistant Professor, Department of Cereal Chemistry and Technology, North Dakota State

Spaghetti was dried in an experimental pasta dryer with an 18-hr. drying cycle (4). During the drying period, the humidity of the dryer was decreased linearly from 95 to 60% r.h. while the temperature was held constant at 38°C.

Isolation of the Wheat Components

Starch, water-soluble pentosans, and water-insoluble sludge pentosans were isolated from semolina and spaghetti according to the procedure of Medcalf et al. (5). Both the semolina and spaghetti were ground prior to isolating the various constituents by passing them through a Brabender Quadruplex micromill. For the dough and wet spaghetti samples the starch was isolated immediately and air-dried prior to analysis.

Starch

Starch pasting properties were obtained using the carboxymethyl cellulose (CMC)- amylograph technique introduced by Sandstedt and Abbott (6) and described by Medcalf and Gilles (7). The water-binding capacity of the starches was determined by the procedure described by Medcalf and Gilles (7). Starch damage in the samples was measured according to the colorimetric method of Williams and Fegol (8). Damaged starch values were expressed as Farrand Equivalent Units by the use of a regression equation. The correlation coefficient between the colorimetric procedure and that of Farrand was 0.95, as calculated by Williams and Fegol (8).

Free Sugars

Free sugars were extracted from semolina and spaghetti by the ternary solvent system of Ponte et al. (9), with the quantitative values for the individual sugars reported in this study being obtained with the Technicon Sugar Auto-Analyzer, following the procedure given by Abou-Guendia and D'Appolonia (10). Glucose was determined quantitatively by the glucose oxidase assay, following the procedure outlined by Banks and Greenwood (11). The amount of glucose and maltose was measured also utilizing the method of quantitative thin-layer chromatography of Ponte et al. (9).

TABLE I.	SUMMARY	OF DURUM WHEAT STARCH AMYLOGRAMS
		INCORPORATING CMC

Starch Sample	Temperature of Initial Pasting °C.	Peak Height B.U.	15-min. Height B.U.	50° Height B.U.
Semolina				
Leeds	58	420	400	560
Hercules	58	430	400	580
Mindum	58	440	410	580
Leeds ^a	58	425	410	580
Yuma ^a	58	410	390	570
Spaghetti			000	370
Leeds	58	375	330	450
Hercules	58	380	355	540
Mindum	58	400	360	560
Yuma ^a	58	400	380	530

^aSamples obtained from sprouted wheat.

Water-Soluble Pentosans

Water-soluble pentosans were purified with α -amylase according to the procedure of Kündig et al. (12). Pentosans were fractionated on a DEAE-cellulose column and further characterized as described in a previous paper (13).

Water-Insoluble Pentosans

Purification with α -amylase and fractionation on a DEAE-cellulose column of the water-insoluble sludge pentosans was performed as outlined by Medcalf et al. (5). The five DEAE-cellulose fractions were then further characterized by paper and gas chromatography as described for the water-soluble pentosans.

RESULTS AND DISCUSSION

Starch

Gelatinization data for durum starches isolated from semolina and spaghetti and utilizing the incorporation of CMC are summarized in Table I. Typical curves, corrected for CMC, for semolina and spaghetti starch isolated from one cultivar (Leeds) are shown in Fig. 1. Semolina starch had a higher peak viscosity than the starch isolated from spaghetti. This decrease in peak viscosity as a result of processing indicated that starch damage occurred to some extent during processing. The values measured for starches isolated from sprouted samples of wheat indicated that differences in gelatinization caused by sprouting were minimal.

The results of experiments on water-binding capacity and starch damage are reported in Table II. Higher water-binding capacity values were obtained for the starches isolated from the spaghetti. These results are in agreement with data obtained for starch damage. The starch damage values revealed that during pasta

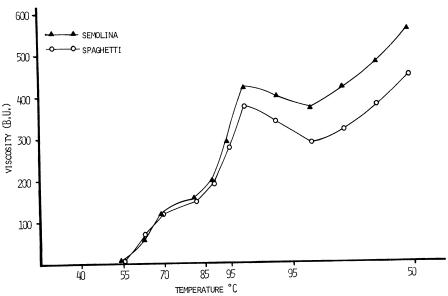


Fig. 1. A comparison of CMC-amylogram curves of starch isolated from Leeds semolina and spaghetti (corrected for viscosity of CMC).

TABLE II.	STARCH DAMAGE AND WATER-BINDING CAPACITY OF
	SEMOLINA AND SPAGHETTI STARCH ^a

_	Starch	Water-Binding	
Source	Whole Sample f.e.u. ^b	Isolated Starch f.e.u.b	Capacity %
Semolina			
Leeds	12.36	1.24	82.0
Hercules	15.38	1.42	82.0
Mindum	11.60	1.67	83.0
Leeds ^C		2.97	83.5
Yuma ^C Spaghetti		2.97	84.5
Leeds	32.31	4.58	91.0
Hercules	30.72	4.13	91.0 87.0
Mindum	30.72	5.49	94.0
Yuma ^c		10.92	91.0

 $^{^{\}rm a}_{\rm k}{\rm Values}$ reported are an average of duplicate determinations.

TABLE III. STARCH DAMAGE VALUES OF DURUM WHEAT PRODUCTS AND ISOLATED STARCHES DURING PROCESSING^a

	Starch	Damage
Source	Whole Sample f.e.u. ^b	Isolated Starch f.e.u. ^b
Semolina Dough Wet spaghetti Dry spaghetti	10.34 8.08 17.26 29.97	1.19 1.37 1.47 2.87

^aValues reported are an average of duplicate determinations expressed on a dry matter basis.

processing the percentage of damaged starch was greatly increased. A certain degree of variability among the different wheat varieties was noted, but in all cases the amount of starch damage in spaghetti was much higher than in the corresponding semolina. The increase in starch damage could be ascribed to one or several of the following causes: 1) mechanical damage occurring during mixing; 2) mechanical damage occurring in the extruder head (because the shearing action of the screw forces the dough against the die); or 3) activity of amylolytic enzymes during processing, and particularly during the drying step. For further investigation, a sample of commercial semolina was processed into spaghetti under standard operating conditions, and samples were taken at different stages during the process: after mixing (dough), after extruding (wet spaghetti), and after drying (dry spaghetti). The percentage of damaged starch was measured and the results are presented in Table III. Under the experimental conditions used, a certain amount of starch was damaged during the extruding phase of processing, but the greatest change occurred during the drying step.

These results indicate that starch mechanically damaged during milling and during the first steps of processing provided a suitable substrate for amylolytic

bFarrand Equivalent Units.

^CSamples obtained from sprouted wheat.

bFarrand Equivalent Units.

enzymes during the drying period. During the initial stages of spaghetti drying, the conditions of humidity and temperature are ideal for enzymatic activity, and as a result the amylolytic enzymes were probably responsible for the observed increase in solubilized starch.

The samples of commercial semolina, dough, and wet and dry spaghetti were also utilized for investigating the change in free sugar content throughout the process. The dough and wet spaghetti samples were freeze-dried prior to sugar extraction. The results of this experiment are reported in Table IV. As evident from the data, the amount of maltose did show a moderate increase after mixing (dough) and a larger increase after extruding (wet spaghetti). No change was observed after drying. The change in glucose, on the other hand, took place mainly during drying. These results confirm that starch was damaged during the mixing and extruding phases of processing, resulting in the release of free maltose. During drying, more maltose was produced by the action of amylolytic enzymes, but any additional increase in maltose was masked by the simultaneous conversion of maltose into glucose, as shown by the increase in glucose during that phase of processing.

The amount of glucose and maltose present in semolina and spaghetti was measured by preparative thin-layer chromatography. Glucose was measured also by the glucose oxidase assay. The results of both experiments were in good agreement with those reported in Table IV.

Water-Soluble and Water-Insoluble Pentosans

The yield of water-soluble and water-insoluble pentosans isolated from semolina and spaghetti and purified with α -amylase is reported in Table V. It is evident that the yield of purified water-soluble pentosans isolated from spaghetti is much higher

TABLE IV. DURUM WHEAT FREE SUGAR CHANGES AT DIFFERENT PROCESSING STAGES^a

Source	Sucrose %	Raffinose %	Maltose %	Fructose %	Glucose %
Semolina	0.40	+	0.15	trace	0.10
Semolina ^b	0.43	+	0.14	trace	0.09
Dough ^b	0.51	+	0.41	trace	0.14
Wet spaghetti b	0.41	+	0.96	trace	0.15
Dry spaghetti	0.45	+	0.97	trace	0.27

^aCommercial blend, containing 85% Leeds.

TABLE V. YIELD OF WATER-SOLUBLE AND WATER-INSOLUBLE PENTOSANS ISOLATED FROM SEMOLINA AND SPAGHETTI AND PURIFIED WITH $\alpha\textsc{-}\text{AMY}$ LASE

Source	Purified Pentosan %
Water-soluble pentosans	0.00
Semolina	0.36
Spaghetti	0.49
Water-insoluble pentosans	
Semolina	0.22
Spaghetti	0.15

bSamples were freeze-dried prior to sugar extraction.

TABLE VI. DEAE-CELLULOSE COLUMN CHROMATOGRAPHY OF WATER-SOLUBLE PENTOSANS

	Fraction	Yield %	Protein %	Ratio Arabinose: Xylose: Galactose		Fraction	Yield %	Protein %	Ratio Arabinose: Xylose: Galactose
Semolina					Spaghetti				
	Unfract.		17.4	1:1.1:0.5	1	Unfract.		9.4	1:1,2:0,4
	1	43.9	2.7	1:1.6: -		1	44.4	0.6	1:1.5: -
	2	14.1	2.2	1:1.3: -		2	21.7	1.4	1:1.4: -
	3	6.0	8.6	1:0.2:1.1	ll .	3	7.3	5.1	1:0.6:0.8
	4	26.7	24.0	1:0.3:1.1	II	4	15.9	18.2	1:0.2:1.3
	5	9.3	33.7	1:1.8:0.1	il	5	10.7	29.7	1:0.3:1.3

TABLE VII. DEAE-CELLULOSE COLUMN CHROMATOGRAPHY OF WATER-INSOLUBLE PENTOSANS

·	Fraction	Yield %	Protein %	Ratio Arabinose:Xylose: Galactose:Glucose		Fraction	Yield %	Protein %	Ratio Arabinose:Xylose: Galactose:Glucose
Semolina					Spaghetti				
	Unfract.	•••	4.8	1:1.1:0.4:1.2	` `	Unfract.		5.3	1:1.1:0.3:0.2
	1	58.0	6.8	1:1.2: - :0.1	11	1	65.9	1.8	1:1.4: - :0.1
	2	6.8	7.4	1:1.1: - :0.5	11	2	9.1	2.1	1:1.2: - :0.1
	3	2.1	8.2	1:1.0:tr.:0.6]]	3	8.3	4.8	1:1.0:tr.:0.2
	4	25.7	5.8	1:0.9:1.7:1.2	H	4	6.4	7.6	1:0.7:1.5:0.3
	5	7.4	7.8	1:1.4:1.9:1.5	11	5	10.3	10.9	1:1.2:1.9:1.3

than that of pentosans isolated from the semolina. The opposite is true for the water-insoluble pentosans. These results confirm the observations of Neukom et al. (14) that during pasta processing insoluble pentosans are degraded by the action of pentosanases, causing an increase in the amount of soluble pentosans. Wolf et al. (15) also reported that the susceptibility of pentosans to the attack by pentosanases may facilitate the isolation of certain cell-wall constituents. In previous papers, Preece and Hobkirk (16,17) similarly reported that changes in the xylan:araban ratio of the pentosan, which alter its solubility, may cause solubilization of initially water-insoluble hemicelluloses.

A comparison of yield, protein content, and ratio of component sugars of water-soluble pentosan fractions obtained by DEAE-cellulose chromatography after isolation from semolina and spaghetti is reported in Table VI. DEAE-cellulose fraction 3 for the spaghetti water-soluble pentosans showed a somewhat lower content of arabinose and galactose. This result might indicate that arabinogalactan chains were partially degraded during processing, and as a result of subsequent dialysis a decrease in the amount of these sugars was observed. The same effect was observed in water-soluble pentosans isolated from bread as compared to the pentosans isolated from the original flour. Yield, protein content, and ratio of component sugars of water-soluble pentosans isolated from semolina and spaghetti processed from sprouted wheat were similarly obtained. The results were quite similar to those reported for the corresponding pentosans derived from sound samples of durum wheat.

Yield, protein content, and ratio of component sugars for the water-insoluble pentosans isolated from semolina and spaghetti following DEAE-cellulose column chromatography are reported in Table VII. Galactose was present in fractions 4 and 5, as well as in the unfractionated material. These results are in agreement with the results of Cole (18) and do not confirm the lack of galactose in the water-insoluble sludge pentosans previously reported by other authors (5,19,20). Glucose was present in the hydrolysates of all the fractions and in the unfractionated material. The amount of glucose associated with spaghetti water-insoluble pentosans was lower than that observed in the pentosans isolated from semolina. The water-insoluble pentosans isolated from spaghetti showed a slight decrease in arabinose, a fact which was mentioned in the discussion of the water-soluble pentosans.

The data obtained for the water-soluble and water-insoluble pentosans indicate that semolina sludge arabinoxylans (fractions 1 and 2) were more highly branched than the corresponding water-soluble arabinoxylans. The higher branching indicates that there were more arabinose side chains on the pentosans isolated from the sludge fraction than from the water-soluble fraction. This result confirms the findings of Montgomery and Smith (19) that pentosans from the water-soluble portion of wheat endosperm may be less branched than the pentosans from the sludge portion of the endosperm. The data obtained do not confirm the conclusions of Medcalf et al. (5) that the degree of branching was similar for water-soluble and sludge pentosans.

Literature Cited

D'APPOLONIA, B. L., GILLES, K. A., OSMAN, E. M., and POMERANZ, Y. Carbohydrates. In: Wheat: Chemistry and technology, ed. by Y. Pomeranz (Rev.). p. 301. Amer. Ass. Cereal Chem.: St. Paul, Minn. (1971).

- 2. DICK, J. W. The effect of durum sprouting on processing. M.S. thesis, North Dakota State University (1971).
- 3. NORTH DAKOTA STATE UNIVERSITY. Laboratory manual of cereal technology methods. NDSU Dep. Cereal Chem. Technol.: Fargo (1972).
- 4. GILLES, K. A., SIBBITT, L. D., and SHUEY, W. C. Automatic laboratory dryer for macaroni products. Cereal Sci. Today 11: 322 (1966).
- 5.MEDCALF, D. G., D'APPOLONIA, B. L., and GILLES, K. A. Comparison of chemical composition and properties between hard red spring and durum wheat endosperm pentosans. Cereal Chem. 45: 539 (1968).
- 6. SANDSTEDT, R. M., and ABBOTT, R. C. A comparison of methods for studying the course of starch gelatinization. Cereal Sci. Today 9: 13 (1964).
- 7. MEDCALF, D. G., and GILLES, K. A. Wheat starches. I. Comparison of physicochemical properties. Cereal Chem. 42: 558 (1965).
- 8. WILLIAMS, P. C., and FEGOL, K. S. W. Colorimetric determination of damaged starch in flour. Cereal Chem. 46: 56 (1969).
- PONTE, J. G., 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).
- 10. ABOU-GUENDIA, M., and D'APPOLONIA, B. L. Changes in carbohydrate components during wheat maturation. I. Changes in free sugars. Cereal Chem. 49: 664 (1972).
- 11. BANKS, W., and GREENWOOD, C. T. The characterization of starch and its components.

 Part 4. The specific estimation of glucose using glucose oxidase. Staerke 23: 222 (1971).
- KÜNDIG, W., NEUKOM, H., and DEUEL, H. Untersuchungen über Getreideschleimstoffe.
 I. Chromatographische Fraktionierung von Wasserloslichen Weizenmehlpentosanen an Diäthylaminoäthylcellulose. Helv. Chim. Acta 44: 823 (1961).
- 13. LINTAS, C., and D'APPOLONIA, B. L. Note on the effect of purification treatment on water-soluble pentosans. Cereal Chem. 49: 731 (1972).
- 14. NEUKOM, H., KUENDIG, W., and DEUEL, H. The soluble wheat flour pentosans. Cereal Sci. Today 7: 112 (1962).
- WOLF, M. J., MacMASTERS, M. M., and SECKINGER, H. L. Composition of the cementing layer and adjacent tissues as related to germ-endosperm separation in corn. Cereal Chem. 35: 127 (1958).
- 16. PREECE, I. A., and HOBKIRK, R. Non-starchy polysaccharides of cereal grains. V. Some hemicellulose fractions. J. Inst. Brew. (London) 60: 490 (1954).
- 17. PREECE, I. A., and HOBKIRK, R. Non-starchy polysaccharides of cereal grains. VII. Preliminary study of pentosan enzymolysis. J. Inst. Brew, (London) 61: 393 (1955).
- 18. COLE, E. W. Isolation and chromatographic fractionation of hemicelluloses from wheat flour. Cereal Chem. 44: 411 (1967).
- 19. MONTGOMERY, R., and SMITH, F. The carbohydrates of the Gramineae. V. The constitution of a hemicellulose of the endosperm of wheat (Triticum vulgare L.). J. Amer. Chem. Soc. 77: 2834 (1955).
- 20. UPTON, E. M., and HESTER, E. E. Nonstarchy polysaccharides and proteins of soft wheat flour tailings. Cereal Chem. 43: 156 (1966).

[Received October 27, 1972. Accepted March 23, 1973]