Basis for Hardness in Pearl Millet, Grain Sorghum, and Corn[1]

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ABSTRACT

A chemical approach was used to study hardness of pearl millet, grain sorghum, and corn. Grits from the three grains were treated with solvents, and the hardness of the residual material was determined using a particle-size index test. The results indicated that 60% tertiary-butanol was more effective than other solvents in making both millet and corn soft and easy to grind. However, *t*-butanol was not effective with grain sorghum. A combination of *t*-butanol and sodium bisulfite or mercaptoethanol was required to soften sorghum grits. When that combination was used with corn, the grits became softer; 78% of the material passed through a 100-mesh (150-μm) sieve. The solubles removed from the grains were added to starch and made into pellets. The pellets were dried and their strength measured with an Instron machine. The solubles extracted with those solvents that were effective in softening the grain produced strong pellets. The force required to break a pellet was directly related to the amount of solubles used to make it. When the solubles were heated before they were added to starch, they lost their ability to hold the starch together. The results show that the substance or substances responsible for hardness in those grains are extractable and sensitive to heat.

Grain hardness affects both the milling behavior and the end use of grain. Millers are interested in hardness because it affects the sieving behavior, energy consumption, fineness of the finished product, and, most importantly, the milling extraction (Tran et al 1981, Moss et al 1980, Symes 1969). The degree of hardness often determines the use of the grain (Simmonds 1974). Durum wheats are suitable for pasta products and soft wheats for cookies. Wheats of intermediate hardness are used for bread. Several baking quality characteristics have been related to hardness, such as the difference in farinograph absorption, mixograph curve height, starch damage, dough-handling properties, and gassing power (Moss 1978, Baker and Dyck 1975, Symes 1969).

There is no simple definition for hardness; several arbitrary definitions form the basis of various hardness tests. Since a rapid, simple, inexpensive way to distinguish between samples has been sought, many tests have been developed. The use of stylus penetration (Katz et al 1961), pearling tests (Taylor et al 1939, Beard and Poehlman 1954), particle-size index (PSI) (Symes 1961, 1965), and compression tests (Tran et al 1981) have been reported. Also, the time required to grind the grain has been used as a measure of hardness (Kosmolak 1978, Greenaway 1969). All those tests for hardness responded in different ways to changes in grain size, protein, and moisture content. However, the PSI test and the pearling resistance test are widely used. They are simple, have the best differentiating abilities, and correlate well with each other (Chesterfield 1971). A good correlation between PSI and near-infrared reflectance at 1,680 nm was partially explained by difference in kernel texture (Bruinsma and Rubenthaler 1978).

Despite the substantial number of reports that deal with techniques to measure hardness, only limited data are available on the factors responsible for hardness in cereal grains. Most of these reports deal with the hardness of wheat.

It was long accepted that vitreousness and hardness were associated, but many investigators have pointed out that the relationship between the two does not always hold (DeFrancisco et al 1982, Simmonds 1974, Beard and Poehlman 1954). Greer et al (1951) found that the endosperm of hard wheats, of either vitreous or mealy grain, broke along the lines of the cell walls, whereas the endosperm of soft wheat broke in a random fashion with the cells being disrupted.

Most investigators agree that the role of protein content in grain hardness is minor. The effect of protein varies from one variety to another (Moss et al 1980, Symes 1965).

MacRitchie (1980) reviewed and criticized the two theories proposed to explain hardness in wheat. One theory is based on the continuity of the protein matrix and the physical contact between starch and protein (Stenvert and Kingswood 1977, Moss et al 1980). A continuous protein matrix, which physically traps the starch granules, would result in difficulty in separating starch from protein and make the grain harder. The other theory, a chemical explanation, relates hardness to the adhesion or the bond between starch and protein (Simmonds 1972, Simmonds et al 1973, Hoseney and Seib 1973). The second theory suggests that in wheat a water-soluble material surrounding the starch granule is responsible for the adhesion of the protein matrix to the starch (Barlow et al 1973). That material is present in greater quantities in hard wheat than in soft wheat.

In this study a chemical approach was used to explain what causes hardness in such cereal grains as pearl millet, grain sorghum, and dent corn.

MATERIALS AND METHODS

Materials

The samples used in this study were: pearl millet, a composite sample of lines (79-2216 × 78-7024 and 79-2201 × 78-7024) grown in Hays, KS, in 1980; grain sorghum (Dekalb F 67), grown in Hays, KS, in 1980; commercial yellow dent corn, grown in Kansas in 1981; and hard red winter wheat, a composite of cultivars grown in Kansas.

All samples were cleaned on the model XT2 Carter dockage tester (Hard-Carter Co., Minneapolis, MN). The light debris was removed with a model FC9 Kice Aspirator (Kice Metal Products, Co., Wichita, KS).

Preparation of Grits

Grits, which are large particles of endosperm −20W + 28W (−841 + 594 μm), were used in this study instead of whole grains so that hardness of the endosperm could be studied without being affected by germ and bran.

Grits were prepared from pearl millet and grain sorghum according to the procedure previously described (Abdelrahman et al 1983). Corn grits were prepared according to the flow shown in Fig. 1.

Chemical Treatments

Grits from the three cereal grains were treated with different solvents and reagents. Those included water, ethanol, tertiary butanol, 2-mercaptoethanol (ME), sodium bisulfite ($NaHSO_3$), salt (0.5% NaCl), and reagents to alter pH. In addition, germinated millet flour (0.5%) was added. The treatment involved soaking the grits in the solvent for at least 6 hr (Badi et al 1978). The ratio of solvent to meal was 4:1 (v/w) unless otherwise specified. The solubles were removed by centrifugation (20 min, 1,000 × *g*) at the end of the soaking period and the treated grits were air-dried at room temperature. Then the grits were tested for hardness as

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described below. The supernatants (solubles) were lyophilized and saved to be used in the compressibility test.

Estimation of the Hardness

The PSI was used for the determination of hardness. In this test a weighted sample (100 g) was ground in a Stein mill, model M1 (Fred Stein Laboratories, Inc., Atchison, KS) for 30 sec and sifted in an Alpine Air-Jet Sifter, model A200LS (Alpine AG Machines, Augsburg, West Germany), for 3 min. The weight of the fraction that passed through the 100-mesh (150-μm) sieve was expressed as a percentage of the initial sample weight and defined as PSI. A high value of PSI signifies a soft material.

Compressibility Test

To determine whether the extracted material contained the cementing substance or substances responsible for hardness, small pellets (1.3-cm diameter, 0.3-cm thickness) were made by dissolving the solubles in a small quantity of the solvent and adding to the starch. Commercial samples of corn and wheat starches were used. A Parr Pellet Press (Parr Instrument Co., Moline, IL) was used to make the pellets. The strength of each pellet was measured after they were dried at room temperature. An Instron Universal Testing machine, model 1132, equipped with a recorder was used for testing the compressibility of the pellets. The head speed of the Instron was set at 5 cm/min, and a compression cell with a maximum load of 5 kg was used.

RESULTS AND DISCUSSION

The effect of several treatments on the hardness as measured by PSI was studied. The following treatments were found to have no effect on hardness: hydration with water followed by drying at room temperature; removal of the water solubles; addition of salt (0.5% NaCl) to the water; addition of germinated millet flour (0.5%) to the water; and changing pH.

The first two treatments suggest that the substance or substances responsible for hardness were not affected by water, while the addition of germinated flour and change of the pH indicate that no enzymatic reaction was involved. The results agree with previous work (Abdelrahman et al 1983) showing that tempering was not beneficial in producing fine particle size from millet grits.

Pearl Millet

Ethanol has been used as a solvent for certain protein fractions (Jones and Beckwith 1970). The effect of ethanol treatment on the PSI of pearl millet is shown in Table I. Both the meal-to-solvent ratio and the ethanol-to-water ratio were varied. The results show that aqueous ethanol was somewhat effective in reducing the particle size of millet grits. The effect of aqueous ethanol was more pronounced at high temperature with an optimum ethanol concentration of 60–70%. The removal of the ethanol solubles from the grits before drying gave no advantage over leaving the solubles with the grits.

Tertiary-butanol is another solvent that was reported to be more effective than ethanol in solubilizing certain proteins (Jones and Beckwith 1970). Its superiority was attributed to its greater hydrophobic character. When t-butanol was used to treat pearl millet grits, it was found to be more effective than ethanol in reducing particle size (Table II). The most effective concentration was 50–60% at room temperature and with four volumes of solvent. The PSI for t-butanol treatment at those conditions was 50%, compared with 39% for the aqueous ethanol treatment. Unlike ethanol, the removal of the solubles from the grits before drying made them much softer. Presumably with ethanol, the solubles were denatured and therefore lost their ability to hold the material together. Thus, the presence or absence of the ethanol solubles had no effect on the hardness of the material. When the grinding time was increased from 30 to 90 sec, 87% of the material passed through the 100-mesh (150-μm) sieve (Table II).

Grain Sorghum

The effect of several solvents and reagents on the hardness of grain sorghum is shown in Table III. Ethanol, isopropanol,

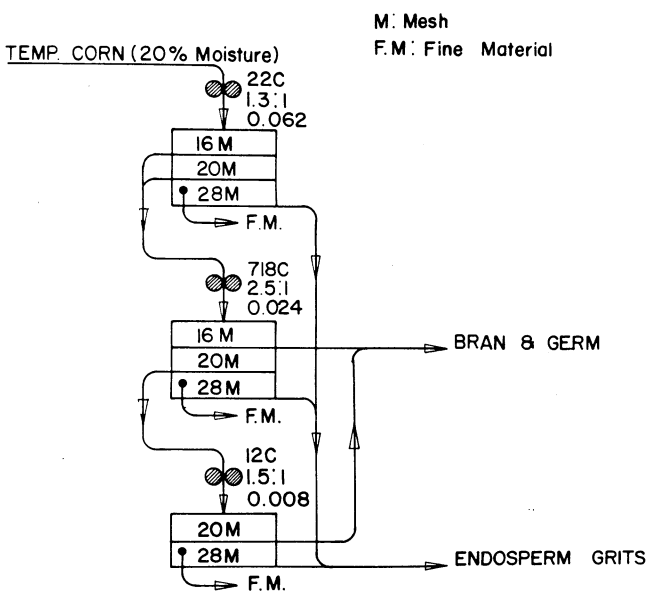

Fig. 1. Scheme for producing corn grits.

TABLE I
Treatment of Pearl Millet with Ethanol[a,b]

Ethanol Concentration (40°C)		60% Ethanol/Meal		60% Ethanol (4 v/w)	
Percent	PSI (%)	v/w	PSI (%)	°C	PSI (%)
50	32.4	1[a]	38.6	25	38.6
70	45.8	2	35.3	40	45.8
80	44.5	4	38.9	...	...
...	...	6	38.7	...	...

[a]Solubles were not removed.
[b]Particle-size index (PSI) for untreated millet 27.3.

TABLE II
Treatment of Pearl Millet with t-Butanol

t-Butanol Concentration (4 vol)		60% t-Butanol/Meal		Grinding Time	
Percent	PSI[a] (%)	v/w	PSI[a] (%)	Sec	PSI[a] (%)
50	50.2	1[b]	38.4	30	49.6
60	49.6	4	49.6	60	67.4
70	47.7	8	47.4	90	86.8
100	32.9	...	...	...	...

[a]Particle-size index.
[b]Solubles were not removed.

TABLE III
Treatment of Grain Sorghum with Different Solvents

Solvent	PSI[a] (%)
Untreated	24.1
60% Ethanol	25.8
60% Isopropanol	26.1
60% t-Butanol	26.9
+ ascorbic acid	25.3
+ cysteine	25.9
+ 0.6% mercaptoethanol	53.1
+ 0.5 $NaHSO_3$	63.7
0.5% $NaHSO_3$ in H_2O	38.4

[a]Particle-size index.

t-butanol, ascorbic acid, and cysteine all had no effect on the particle size distribution of sorghum. However, addition of $NaHSO_3$ or ME to aqueous *t*-butanol gave a large increase in the PSI of sorghum grits, indicating that the material had become softer. Both $NaHSO_3$ and ME are known to be effective in breaking disulfide bonds. Grain sorghum endosperm contains significant amounts of proteins that are alcohol soluble after the disulfide bonds have been reduced (Guiragossian et al 1978). Nwasike et al (1979) found that sorghum is unique among cereals in its high level of that prolaminelike fraction (cross-linked kafirins). The protein components of that fraction contain mostly intramolecular disulfide bonds (Sastry and Virupaksha 1969). Reduction of the disulfide bonds produces molecules resembling the native sorghum prolamines in their properties.

Clearly that prolaminelike fraction in grain sorghum is related to the hardness of the grain (Table III). When $NaHSO_3$ or ME was used in water instead of *t*-butanol, their effect on hardness was much less pronounced.

Corn

The effect of *t*-butanol on corn grits was similar to that on pearl millet (Table IV). Both grains became softer after treatment, as indicated by the increase in PSI. Treating the material with the solvent more than once did not have any advantage.

Unlike pearl millet, the PSI for corn was greatly increased when the grits were treated with a combination of $NaHSO_3$ and aqueous *t*-butanol. The material became so soft that 78% of it passed through the 100-mesh (150-μm) sieve. The effect of sodium bisulfite with corn may be similar to its effect on grain sorghum. Corn also contains a prolaminelike fraction similar to the one in sorghum (Misra et al 1973, Robutti et al 1974), but the level of those proteins is much less. The removal of both the prolamine and the cross-linked prolamine fraction made corn very soft and easy to grind to a fine particle size.

Contrary to the result with the three cereal grains above, treating wheat (HRW) with *t*-butanol made it slightly harder (Table IV).

TABLE IV
Treatment of Cereal Grains with 60% *t*-Butanol[a]

Cereal Grain	Untreated (PSI, %)[b]	Treated Once (PSI, %)[b]	Treated Twice (PSI, %)[b]	*t*-Butanol + 0.5% $NaHSO_3$ (PSI, %)[b]
Pearl millet	27.3	49.6	51.7	52.8
Corn	27.8	51.3	56.5	77.8
Grain sorghum	24.1	25.5	26.9	63.7
Wheat (HRW)	31.9	25.0	...	...

[a]Four volumes at room temperature.
[b]PSI = particle-size index.

TABLE V
Compressibility of Pellets Made From Solubles and Starch Using an Instron

Solubles Source	Percent Solubles	Starch	Force (kg) to Break the Pellet
Corn			
60% *t*-Butanol	1	Corn	2.7
	2	Corn	3.5
	2	Wheat	3.7
	5	Corn	7.9
	5	Wheat	14.7
	10	Corn	18.1
Boiled 60% *t*-butanol	10	Corn	0
Sorghum			
60% *t*-Butanol	10	Wheat	1.5
60% *t*-Butanol + $NaHSO_3$	10	Wheat	28.7
Boiled 60% *t*-butanol + $NaHSO_3$	10	Wheat	0
Pearl millet			
60% *t*-Butanol	10	Wheat	6.6
Boiled 60% *t*-butanol	10	Wheat	0

That may be because the drying effect of the alcohol strengthens the water-soluble bond between the starch and protein (Simmonds et al 1973).

Compressibility Test

The previous experiments indicated that treating cereal grains with certain solvents made them softer and easier to grind. However, those experiments did not clearly show why the material became softer. A reasonable assumption would be that the substance or substances responsible for hardness had been solubilized with the solvent. If that were true, then adding the extracted solubles back to the residual material would restore hardness. However, adding the solubles to the residual material does not ensure that the solubles will return to the place from which they were extracted. Results obtained from adding the soluble to the residual material were, in fact, not reproducible. To avoid that difficulty, the solubles were added to wheat starch, and the mixture was formed into pellets.

Pellets made from aqueous *t*-butanol solubles of corn were very hard, and only a large force would break them (Table V). The force required increased as the amount of solubles from which the pellet was made increased. That was also true when corn starch was used instead of wheat starch. It was not clear why more force was required to break pellets made with wheat starch.

Pellets made from aqueous *t*-butanol solubles of sorghum would break with a small force, whereas pellets made from the aqueous *t*-butanol $NaHSO_3$ solubles and starch required a large force (Table V). Those results are consistent with the previous finding that aqueous *t*-butanol alone had essentially no effect on sorghum hardness, and the addition of $NaHSO_3$ was necessary to produce soft grain. The results also support the assumption that the solvents act by solubilizing substances responsible for hardness. The results also show that the reduced cross-linked prolamines (kafirins) do not have the same properties as prolamines.

Heating the solubles before they were added to starch and pelleted produced weak pellets (Table V). Thus, the substances responsible for hardness in those grains are heat sensitive.

SUMMARY AND CONCLUSIONS

A chemical approach was used to study hardness in pearl millet, grain sorghum, and corn. Grits from the three grains were treated with solvents, and the hardness of the residual material was determined using a PSI test. It was found that hydration with water, removal of the water solubles, and addition of salt (NaCl) had no effect on the hardness of the three grains.

The results show that 60% *t*-butanol was more effective than 60% ethanol in making both millet and corn softer and easier to grind. However, neither aqueous *t*-butanol nor ethanol was effective with grain sorghum. Aqueous *t*-butanol containing $NaHSO_3$ or ME did make sorghum soft. The effect of the $NaHSO_3$ and ME apparently is reduction of the disulfide bonds. Hence, the prolaminelike fraction (cross-linked kafirins) in sorghum is related to hardness. When that solvent (*t*-butyl alcohol plus bisulfite $NaHSO_3$ or ME) was used with corn, the grits were softer; but the solvent had no advantage over *t*-butanol alone with millet, as shown in Table 4.

Pellets were made from starch and the soluble fractions. The force required to break the pellets was directly related to the amount of solubles used and the source of the solubles. The solubles extracted with certain solvents that were effective in softening the grain produced pellets with good strength. Heating the solubles before they were added to starch caused them to lose their ability to hold the starch together. The results show that the substance or substances responsible for hardness in those grains are extractable and sensitive to heat.

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