NMR-OIL CONTENT AS AN INDEX OF DEGREE OF RICE MILLING[1]

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ABSTRACT

Brown rice samples (nine cultivars from three locations) were milled on an experimental mill. Oil in 26 brown rices and in 173 milled subsamples was determined by wide-line nuclear magnetic resonance. Oil content of long- and medium-grain cultivars was not consistently different, but in each group there were consistent varietal differences. Weight loss during milling was significantly correlated ($r = -0.617$) with oil content of the milled samples at the 1% level. Correlation coefficients for samples from individual varieties were generally higher (up to $r = -0.874$) than for all samples combined. Regression coefficients of oil content on milling weight loss for individual varieties ranged from -0.119 to -0.298.

Brown (dehusked) rice is milled to separate the "bran" from the endosperm. Commercial rice bran contains the pericarp (including the tegmen), the embryo, and (in well-milled rice) most of the aleurone layer. The FAO Revised Model System of Grading Rice in International Trade (1) defines four types of milled rice: a) undermilled, in which part of the germ and most (or all) of the pericarp have been removed; b) reasonably well milled, in which the germ and pericarp and most of the aleurone have been removed; c) well milled, in which the germ, the pericarp, and practically all the aleurone have been removed; and d) extra well-milled rice, which contains the starchy endosperm only. Those definitions pertain to the "average" of a sample, so small variations among individual kernels can be tolerated. There is a large price difference between whole-kernel milled rice and broken pieces. Because amount of broken kernels increases rapidly with degree of milling, it is important to control the milling process and develop quick and reliable tests for degree of milling.

Three types of methods are available for estimating degree of rice milling: visual, optical, and chemical. The visual methods, most widely accepted and used, have the usual errors of subjective tests. Most of the optical methods measure reflectance or transmittance properties in the visible range of the spectrum. The results are influenced by the color of the rice as affected by variety, growth conditions, texture, and history of the grain. Those limitations can be reduced somewhat by visual (or optical) observation of kernels immersed in dye solutions that preferentially stain the bran layers. Determining optical properties in the far-red (660 nm) or near-infrared (850 nm) eliminates some of the interferences encountered in measurements in the visible range, but the results are affected by moisture, heat damage, chalkiness, and age of the grain (2).

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Chemical methods are based on measuring a component that is more concentrated in bran tissues than in the starchy endosperm. Components proposed for measuring include crude fiber (3), ash (4) and ash components (3,5,6,7), proteins (8), thiamine (5,6), and oil (5,9,10). Determination of either surface oil or total oil has been recommended. Determining surface oil is an empirical method that measures only the exposed portion of oil in the germ and aleurone rather than the total amount of residual oil. Determining the total oil content is a satisfactory index of rice milling because of the high concentration of oil in the germ and aleurone, but the classical determination of total oil is even more complex and time-consuming than that for surface oil.

Wide-line nuclear magnetic resonance (NMR) spectroscopy has been used to analyze oil in seeds and has opened new opportunity for geneticists and plant breeders. The method is nondestructive, rapid (about 2 min excluding drying time), and can be used to determine the oil content of a single seed or of a bulk sample (11). The measured NMR value is related to the total hydrogen in the oil fraction of the seed, independent of the hydrogen in the nonoil fraction. The oil content is calculated from calibration tables or curves. The method has been used successfully to assay oil in corn (12), soybeans (13,14), and other oil-containing seeds (15).

This report describes the use of the NMR method to determine oil in rice as an index of degree of milling.

MATERIALS AND METHODS

The 26 rough rice samples from three locations (Stuttgart, Ark.; Crowley, La.; and Beaumont, Tex.) included four medium-grain (Brazos, Nato, Saturn, and Vista) and five long-grain cultivars (Bluebelle, Bonnet 73, Labelle, Lebonnet, and Starbonnet) (Table I).

The rice samples (160 g) were husked on a McGill laboratory sheller and milled

TABLE I
Description of Rice Samples

Variety	Type	No. of Brown Rices	Average Varietal Oil Content of Brown Rice[a] %	No. of Subsamples Milled from the Brown Rices	Ranges of Varietal Weight Loss in Milling of Brown Rices %
Brazos	Medium	3	2.77	25	3.22–13.55
Nato	Medium	3	2.80	23	2.61–13.61
Saturn	Medium	3	3.14	23	1.99–15.45
Vista	Medium	3	2.95	13	3.98–13.43
Bluebelle	Long	2	2.88	6	4.39–14.63
Bonnet 73	Long	3	3.21	20	1.82–11.93
Labelle	Long	3	2.78	25	1.16–14.03
Lebonnet	Long	3	3.03	18	2.61–12.84
Starbonnet	Long	3	3.04	20	3.21–11.17

[a] Determined by NMR on rice dried to a 5% moisture level.

on a McGill laboratory miller No. 2. The moisture contents of the husked samples ranged from 15.1 to 17.2%.

These moistures are somewhat higher than those usually found in commercial rice milling. Moisture at milling is known to affect milling results as measured by breakage. The higher moisture contents and the variation in moisture may have affected breakage during milling and accounted for part of the variation and amount of milling losses.

By varying the setting on the mill arm (no weight to weight full length of bar), and the milling time (30 to 120 sec), each sample of brown rice was milled to give up to seven subsamples representing different degrees of milling; 173 subsamples were milled. Weight loss in milling was the difference between weight of whole-kernel brown rice and weight of whole-kernel milled rice in the sample. Only whole kernels were included in the analysis to exclude the weight loss associated with breakage during milling.

Oil content was determined by the wide-line NMR method of Alexander *et al.* (12). The NMR method requires drying the samples to 5% moisture prior to analysis to eliminate the effects of the water hydrogen. A calibration equation (% oil = 0.083 NMR signal + 0.44) was developed for converting NMR integrator signals to per cent oil by the method of Conway and Earle (16).

RESULTS AND DISCUSSION

The average (varietal) oil content of the brown rice samples (dried to about 5% moisture prior to oil determination by the NMR method) ranged from 2.77 to 3.14% for medium-grain cultivars and from 2.78 to 3.21% for long-grain cultivars (Table I). Apparently, the range and average oil content of the medium- and long-grain cultivars did not differ greatly. However, in each group one cultivar consistently contained more oil than another; *i.e.*, Saturn *vs*. Brazos among medium-grain and Bonnet 73 *vs*. Labelle among the long-grain rices.

The weight distribution of various tissues in the brown rice is 1 to 2% pericarp,

TABLE II
Statistical Analyses of Relation between Weight Loss and Oil Content

	All Samples			**Excluding Brown Rice**		
Variety	**Correlation coefficient**	**Regression equation**	**Standard error of estimate**	**Correlation coefficient**	**Regression equation**	**Standard error of estimate**
Brazos	−0.797**	2.614−0.168X	0.511	−0.657**	2.439−0.150X	0.536
Nato	−0.842**	2.947−0.180X	0.461	−0.787**	3.445−0.238X	0.477
Saturn	−0.901**	3.263−0.218X	0.422	−0.869**	3.365−0.230X	0.446
Vista	−0.591*	3.188−0.088X	0.532	−0.589*	3.479−0.119X	0.556
Bluebelle	−0.910**	3.024−0.155X	0.339	−0.874**	3.209−0.174X	0.358
Bonnet 73	−0.688**	2.813−0.218X	0.750	−0.483	2.404−0.161X	0.774
Labelle	−0.739**	2.999−0.165X	0.631	−0.661**	3.380−0.200X	0.657
Lebonnet	−0.707**	2.867−0.154X	0.421	−0.787**	3.415−0.212X	0.447
Starbonnet	−0.905**	3.255−0.260X	0.455	−0.863**	3.585−0.298X	0.471
All samples	−0.738	2.939−0.173X	0.626	−0.617	2.934−0.173X	0.667

4 to 5% aleurone plus testa, and 2 to 3% germ (17), and the bran tissues comprise 7 to 11% of the brown rice. Generally, samples with the smallest milling loss are those from which primarily the pericarp was removed and samples with the largest milling loss are the fully milled rices. The weight loss of the least milled samples ranged from 1.16 to 7.82% (average 4.5%); those samples contained 1.54 to 3.22% oil. The weight loss in the most fully milled samples ranged from 5.48 to 15.45% (average 11.8%); those samples contained 0 to 1.16% oil (average 0.56%). Those wide ranges in milling loss and oil content resulted both from large variations in milling response of the brown rice samples subjected to similar treatment and from the large variations incurred during experimental milling.

Despite those inherent sources of error of the experimental milling procedure, the relations between weight loss and oil content were computed (Table II). Those relations are given for the individual varieties and for all samples, in each case including and excluding the brown rice samples. The correlation coefficients were consistently higher for the series with than for the series without the brown rice samples. This difference is attributed to the high oil content of the brown rice, which increases the range of analytical values. Slopes of regression lines for percentage oil on weight loss varied widely among cultivars, from −0.119 for Vista to −0.298 for Starbonnet, indicating a possible significant difference. The differences could have resulted from differences in oil distribution in the kernel tissues, variations in patterns of tissue abrasion during milling due to differences in grain structure, gross composition, texture, etc., or a combination of those and other factors.

The regression coefficients for data on each variety, both including and excluding data for brown rice, were tested for heterogeneity by an appropriate F test in an analysis of covariance. No heterogeneity was established at the 1 and 5% confidence levels when brown rice data were excluded. That is, the rate of change of per cent oil as a function of weight loss in milling was independent statistically of varietal differences. When brown rice data were included, heterogeneity was established at the 5% level but not at the 1% level. Two varieties, Vista and Bonnet 73, appear to behave differently from the others. Omitting the data for these two varieties, no varietal heterogeneity was established at the 1 or 5% levels.

Since no heterogeneity was established at the 1% confidence level, the data for all varieties were combined and analyzed. The correlation coefficient of −0.617 for all samples (excluding brown rice) is highly significant (at the 1% level) but rather low and explains only about 37% of the variability. Possibly, the large spread of experimental values around the regression line for all samples may be caused by the different varietal responses to milling. This is borne out by the fact that correlation coefficients for seven of the nine varieties were higher than the correlation for the total. In three varieties, the correlation coefficient was over 0.86 and explained as much as 75% of the variability.

Our data indicate that oil determination by the NMR method is a useful index of experimentally milled rice. It is now necessary to establish the commercial value of the NMR-oil method as an index of degree of milling. Such a study is underway.

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