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Quantification of blends of black gram and rice using pentosan as an indicator

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Abstract

Instant mixes for traditional foods, based on blends of rice and black gram flours, are widely available in the Indian subcontinent. However, no analytical methods are as yet reported to determine the blend composition. This work attempts to utilise differences in the pentosan content of rice (0.16%) and black gram (7.41%) as parameters to quantify the blend composition, using a modified bromate/bromide method. The validity of the method was confirmed by using model blends of rice and black gram flours. Analysis of market brands of such mixes using the method revealed that the premixes for *idli, dosa, medu vada* and *papad* flours contained black gram, ranging from 24.5 to 31.0, 28.0 to 31.35, 71.0 to 74.5 and 69.0 to 80.0%, respectively. © 2002 Published by Elsevier Science Ltd.

Keywords: Pentosan; Indicator; Blends; Black gram; Rice

1. Introduction

Instant mixes of traditional products such as *idli, dosa, medu vada*, based on rice and black gram blend flours, are becoming increasingly popular in the Indian market. Due to a large difference in the prices for black gram and other cereals, the manufacturers are tempted to reduce the proportion of black gram in the flour mix while tailoring the texture by use of other processing aids. In view of the proposed labelling of contents of ingredients of such mixes, which is expected to be mandatory in coming years, the non-availability of any method for such an analysis is a cause for concern.

Amongst the non-cellulosic structural polysaccharides present in foods, hemicelluloses, comprising xylans (linear and branched molecules with glucuronic acid and or arabinose side chains), galactomannans and arabinogalactans (Southgate, 1991), contain the pentosans. While rice contains a total of 0.3% non-cellulosic polysaccharides, hemicellulose in black gram is estimated at 10.7% (Kamath & Belavady, 1980; Reddy, Padhye, & Salunkhe, 1989; Reddy, Sathe, & Salunkhe, 1989). Pentosans are generally quantified in wheat flour as an indicator of bran left in the flour along with crude fibre and ash (Hart & Fiesher, 1971). A literature survey of the constituents in rice and black gram shows the former to contain no more than 1–2% pentosans and the latter to be richer in hemicelluloses, although the content of pentosans is not clearly reported in the available literature. Arabinogalactans from black gram have been isolated and characterized (Susheelamma & Rao, 1978) and their role in the texture of leavened products has been ascertained (Sushheamma & Rao, 1979).

Estimation of pentosans is based on the formation of furfural when the pentosans or pentoses are distilled with strong hydrochloric acid. The furfural so obtained is generally quantified gravimetrically, as the weight of the precipitate obtained on reaction with phloroglucinol, barbituric acid or 2,4-dinitrophenylhydrazine, volumetrically using bromate/bromide solution, colorimetrically using aniline acetate or orcinol, and spectrophotometrically (Browning, 1967). Among these methods, the volumetric bromate/bromide method is accepted as official by the American Association of Cereal Chemists (Hart & Fisher, 1971) and is most frequently used. The other methods, listed above, suffer the disadvantage of interference by other constituents present in the experimental sample.

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In the present work, the possibility of using this parameter as an indicator of the black gram content in such mixes was explored.

2. Materials and methods

2.1. Materials

Five different samples of dehulled black gram dal (*Phaseolus mungo*) and parboiled rice (*Oryzae sativa*), each, were collected from the local market. All chemicals and solvents used were of AR Grade. Samples of instant mixes of *idli, dosa, medu vada* and black gram *papads*, of different commercial brands, were obtained from the local market of Mumbai city.

2.2. Methods

2.2.1. Preparation of blends of flours of black gram dal and parboiled rice

Black gram and parboiled rice were ground through Tecator Cyclotec mill (Sieve size 0.5 mm) to fine flours. Blends of these flours were made in proportions of 100:0, 90:10, ... 0:100 of black gram: parboiled rice (w/w) and mixed thoroughly.

2.2.2. Estimation of total pentosans in the blended flours

The total pentosan content in the flour blends was determined by the volumetric bromate/bromide method (Browning, 1967) as follows: to 1 g of the sample (known moisture content) prepared as in (a), above, in a 500 ml distillation flask, 100 ml of 12% HCl was added by washing all the sample to the bottom. The liquid level was marked on the flask. A few glass beads were added, and the condenser attached to the flask. Three hundred millilitres of 12% HCl was added to a separating funnel, which was attached to the distillation flask, which was heated electrically.

The distillate receiver (500 or 1000 ml) was placed in an ice bath to prevent escape of furfural. The distillation was carried out at a rate of about 50 ml per 15 min and a total of 300 ml of distillate was collected. During the distillation, the volume was maintained at the original 100 ml level in the flask by adding HCl from the separating funnel. The condensate was transferred to a 1 l glass-stoppered flask and 50 ml distilled water and 250 g crushed ice made from distilled water were added. After the temperature fell to 0 °C, 20 ml of of 0.2N bromate/bromide solution (Browning, 1967) was added with minimum agitation; the flask was stoppered promptly, shaken well and allowed to stand exactly for 5 min; 10 ml of 10% potassium iodide solution were then added and the mixture shaken so as to allow adsorption of bromine vapour. The content of the flask was then titrated with 0.1N sodium thiosulphate solution using starch as an indicator. A blank titration was performed simultaneously. The total pentosan content was calculated by using the formula

$$\%\text{Pentosan content} = \frac{7.5 \times N \times (V_2 - V_1)}{W} \times \frac{X}{100} \quad (1)$$

where N = normality of sodium thiosulphate solution; V_2, V_1, blank and sample reading, (ml), respectively; W, weight of sample, (g) on moisture free basis; and X = correction factor accounting for the hydroxymethyl furfural produced during distillation. The formula used is a modified version of the original formula used for determination of pentosan in wood samples, i.e.

$$\%\text{pentosan} = \frac{7.5 \times N \times (\mathrm{V2} - \mathrm{V}l) - 1.0}{W} \quad (2)$$

where N = normality of sodium thiosulphate solution; V1 = titration (ml) for test sample; V2 = titration (ml) for blank; and W = weight of moisture free sample.

Subtraction of 1.0 compensates for hydroxymethyl furfural produced during the distillation in the case of wood samples.

The modified formulam, as in Eq. (1) was arrived at as described later in Section 3, on the basis of distribution coefficient (K), described in Section 2.2.3.

2.2.3. Determination of distribution coefficient (K) of pure furfural (F), hydroxymethyl furfural (HMF), and their blends (Bethge, 1958)

It is well known that, on heating in the presence of acid, the pentoses in a sample are converted to furfural (F), and hexoses to hydroxymethyl furfural (HMF) which would therefore be present in the distillate of the sample. Depending on the recovery of F and HMF in the distillate under the given set of reaction conditions, their proportions in the distillate would differ. Therefore it is necessary to ascertain the relative recovery of F and HMF in distillate under a given set of reaction conditions. To this end, a standard pentose, i.e xylose AR, and a standard hexose, i.e glucose AR were used. The difference in the distribution coefficients of the two aldehydes between the chloroform and water phases forms the basis of this method. The sum of the two aldehydes, F and HMF, is expressed as millitres of 0.1N thiosulphate solution used up by the distillate in the volumetric bromate/bromide method (Browning, 1967). Therefore, pure standard xylose and pure standard glucose were mixed in proportions ranging from 100:0 to 0:100. One gram of each of these mixtures was dissolved in 100 ml of 12% HCl and subjected to distillation as described in Section 2.2.2.

One hundred millilitres of the distillates so obtained were shaken with 100 ml of chloroform for 10 min, vigorously. Two layers were allowed to separate. The

upper aqueous layer was collected and titrated against 0.1N sodium thiosulphate as described in (b). The final temperature of the distillate before separation of layers was always maintained at 25 °C.

The distribution coefficients (K) of the blends of the xylose and glucose were calculated as: $K=[A-B]/B$ Where, $A=0.1$N sodium thiosulphate (ml) required for titration of total volume of distillate; and $B=0.1$N sodium thiosulphate (ml) required for titration of total aqueous layer of distillate.

2.2.4. Determination of distribution coefficient (K) of F and HMF derived from black gram and parboiled rice flour blends

One-gram blends of black gram and parboiled rice in the proportions of 0:100, 10:90...100:0, respectively were prepared (using five different samples of black gram and parboiled rice). K values for F and HMF in these black gram and parboiled rice blends were determined as described in Section 2.2.1.

2.2.5. Analysis of market samples of instant mixes of idli, dosa, medu vada and black gram papad for pentosan content

Pentosan content of above market samples of instant mixes was determined as described in Section 2.2.2.

3. Results and discussion

3.1. Distribution coefficient, K of F and HMF in model blends of glucose and xylose

Distribution coefficients (K) of F and HMF, in the distillates of their mixtures were determined using distillates of blends of pure xylose (AR grade) and pure glucose (AR grade) in proportions ranging from 100:0 to 0:100, subjected to titration as described earlier. In order to arrive at the experimental values of F and HMF, the readings obtained for total distillate were substituted in Eq. (2) without any correction factor, as pure glucose or pure xylose were used. The% total F and HMF obtained in the distillate corresponding to the blend of 100:0 of glucose: xylose was taken to have been contributing to 100% HMF and that of 0:100 of glucose: xylose equal to 100% F. However, in the case of blends when distribution coefficients were plotted against % pentose in the glucose:xylose blends, because of the difference in the ability of F and HMF to be distilled out, linearity was not observed (Fig. 1). Using this curve, attempts were made to determine the corresponding correction factor, designated as "X", by drawing an imaginary y' axis parallel to the y axis. The entire curve was equally divided to cover the range of 0–100 as shown in Fig. 1. The values corresponding to different K values on the y axis read on y' axis gave the corresponding correction factor X. Using these, correction factors for % HMF content and % F content of 100:0 glucose:xylose and 100:0 xylose:glucose were established to be 1.62 and 85.9% as expected.

3.2. Distribution coefficient, K of F and HMF in model blends of parboiled rice and black gram

On a similar basis, when the distribution coefficient, K, was plotted for various ratios of parboiled rice and black gram (Fig. 2), a trend similar to that obtained in Fig. 1 was observed. Parboiled rice and black gram showed distribution coefficients of 1.79 and 16.0, respectively. The values corresponding to different K values on the y axis, read on the y' axis gave the correction factor X. Hence to account for the contribution of HMF in the form of a correction factor, designated as X, for calculation of pentosan content of any samples, the Eq. (2) for % pentosan was modified to be:

$$\%\ \text{Pentosan content} = \frac{7.5 \times N \times (V_2 - V_1)}{W} \times \frac{X}{100} \quad (1)$$

Using this modified formula the pentosan contents of parboiled rice, black gram and their blends in various proportions were determined. An excellent correlation ($R^2=0.9986$) between the proportion of black gram in the blend with the pentosan content was observed as seen in Fig. 3. This suggested pentosan to be a correct indicator of black gram content in a blend of parboiled rice and black gram. Using the regression equation obtained ($Y=0.073X+0.226$, where 'Y' and 'X' represent the pentosan content and % black gram in the blend of rice and black gram), the pentosan contents of rice flour and black gram are estimated to be 0.2 and 7.5% respectively. This is in accordance with the literature reports which suggest a total of 0.3% non-cellulosic polysaccharide for rice (Southgate, 1991) and about 10% for black gram (Reddy, Padhye, & Salunkhe, 1989).

3.3. Determination of black gram content in market premixes of traditional foods

For products such as *idli* and *dosa*, which conventionally use 35:65 of black gram parboiled rice or *medu vada*, which use black gram at 90:10 or black gram *papad* which uses black gram at 100% (excluding about 10% of papadkhar and salt), factor X values were then determined on the basis of their distribution coefficients by referring to Fig. 2. In Table 1 these factors are shown. Using these factors, the black gram content of market samples of instant mixes of *idli, dosa, medu vada* and black gram *papad* were determined by using the modified formula. All five samples of each of the above products were found to have black gram contents as

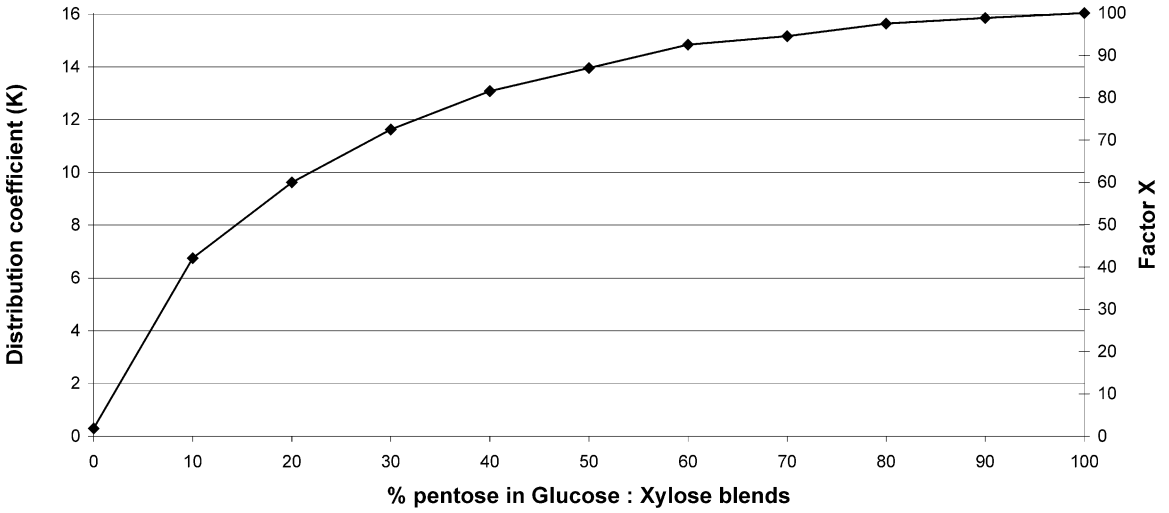

Fig. 1. Distribution coefficient K and factor X, for glucose:xylose blends based on the % pentose content.

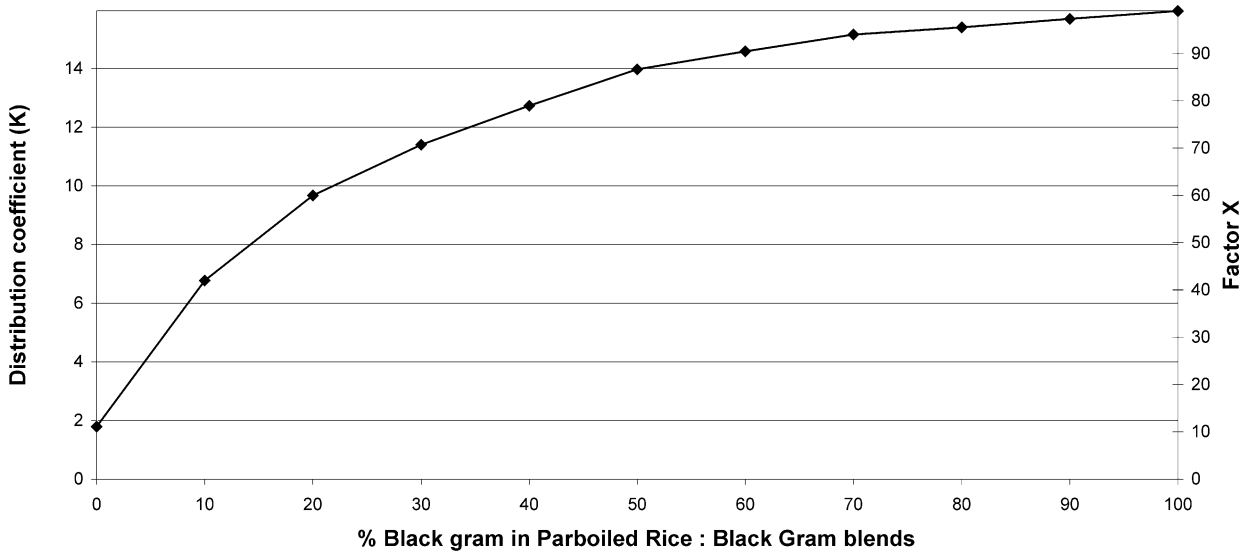

Fig. 2. Distribution coefficient K and factor X, for parboiled rice:black gram blends based on the content of black gram.

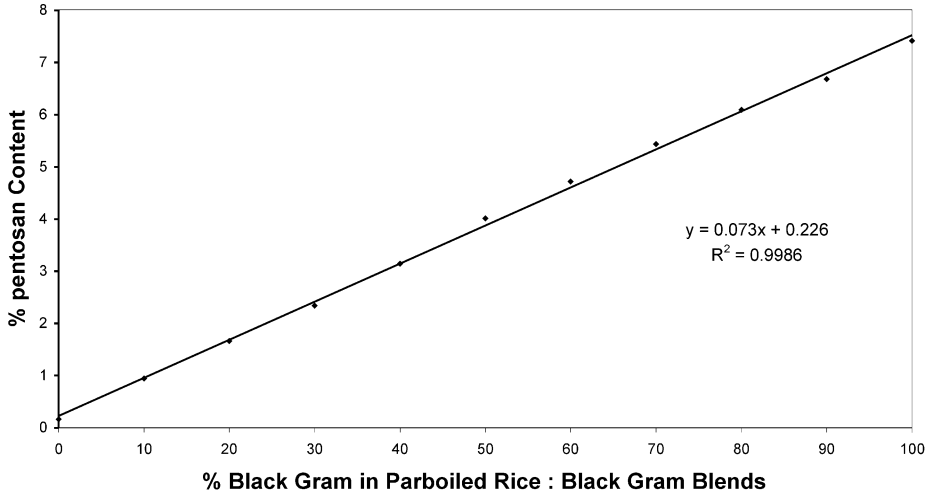

Fig. 3. Percentage of black gram in parboiled rice:black gram blends based on the pentosan content.

Table 1
Factor '*X*' for parboiled rice:black gram-based products

Product	% Black gram[a]	% Parboiled rice[a]	Factor *X*
Idli	35	65	74
Dosa	35	65	74
Medu Vada	90	10	98
Black gram *papad*	100	–	99

[a] Traditionally used proportions.

Table 2
Pentosan content and estimated black gram content of market samples of *idli*, *dosa*, *medu vada* and black gram *papad* premixes

Samples	*X*	% Pentosan[a]	% Black gram[b]
Idli premixes			
1	74	2.41±0.01	30.0
2	74	2.47±0.01	31.0
3	74	2.07±0.02	24.5
4	74	2.22±0.02	26.5
5	74	2.37±0.02	28.5
Dosa premixes			
1	74	2.52±0.01	31.5
2	74	2.36±0.01	28.0
3	74	2.22±0.02	28.5
4	74	2.32±0.02	30.0
5	74	2.26±0.02	29.0
Medu vada			
1	98	5.49±0.01	72.5
2	98	5.61±0.02	74.0
3	98	5.62±0.02	74.5
4	98	5.37±0.01	71.0
5	98	5.53±0.01	73.0
Black gram *papad* premixes[c]			
1	99	6.23±0.01	80.0
2	99	5.47±0.02	72.5
3	99	5.82±0.01	75.0
4	99	5.35±0.02	71.0
5	99	5.22±0.01	69.0

[a] Results are mean±S.D. of three individual determinations
[b] Computed using Fig. 2.
[c] Around 10% of the papad flour is made up of salt and papadkhar.

shown in Table 2, indicating that the manufacturers were using near conventional formulation.

These results indicate the pentosan content to be a very useful calibration method for determination of the black gram content in the blend, which could be used for mandatory labelling within the same batch of the manufactured product.

4. Conclusion

The differences in the pentosan content of black gram and parboiled rice make it a useful indicator of black gram content in products using this legume as a ingredient in the formulation. The validity of the method was confirmed by using model blends of parboiled rice and black gram flours in various ratios. Analysis of market samples of instant mixes of *idli, dosa, medu vada* and black gram *papad* showed manufacturers to be using black gram proportions near authentic formulation.

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