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# Free Sugars and Non-Starchy Polysaccharides of Finger Millet (*Eleusine coracana*), Pearl Millet (*Pennisetum typhoideum*), Foxtail Millet (*Setaria italica*) and their Malts

N. G. Malleshi, H. S. R. Desikachar & R. N. Tharanathan

Central Food Technological Research Institute, Mysore, India

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*ABSTRACT*

*The aqueous ethanol extractable sugars and non-starchy polysaccharides of finger millet, pearl millet, foxtail millet and their malts were isolated and characterised. In comparison with native millets, the malted samples contained significantly higher levels of free sugars (glucose, fructose and maltose) and water-soluble non-starchy polysaccharides (WSNSP). The WSNSP isolated from malted samples were richer in hexoses than pentoses. The yield, as well as the qualitative and quantitative sugar profiles of the hemicellulosic polysaccharides, showed little variation between native and malted millets.*

## INTRODUCTION

In India, the production of minor millets is about 10 million tonnes per annum, almost all of which is utilised as food. Among their many uses, millets are often malted, malted millets being of considerable value in the development of weaning foods (Brandtzaeg *et al.*, 1981; Malleshi & Desikachar, 1982). Free sugars and non-starchy polysaccharides (fibre constituents) are nutritionally important in weaning food formulations (Jansen, 1980). Millet grains are known to contain slightly higher levels of unavailable carbohydrates or non-starchy polysaccharides than wheat or rice (Kamat & Belavady, 1980).



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The malting process essentially involves a controlled germination of the grains, resulting in the elaboration of various carbohydrases with concomitant hydrolysis of seed carbohydrate constituents (Palmer & Bathgate, 1976). Apart from a few reports on the carbohydrate profile of millets (Emiola & De La Rosa, 1981; Monteiro, 1982; Muralikrishna *et al.*, 1982), information on the carbohydrates of malted millets is unavailable. An investigation of this aspect was carried out and the results are reported in this paper.

## MATERIALS AND METHODS

### Malting

Certified varieties of finger millet (*Eleusine coracana*), Indaf-6, pearl millet (*Pennisetum typhoideum*), Co-6, and foxtail millet (*Setaria italica*), Si-76/4, identified as possessing superior malting characteristics (Malleshi, 1984), were used. Seeds were steeped in water for 24 h and germinated for 48 h at 25 °C in a B.O.D. incubator. Finger millet seeds were also germinated for 96 h in order to obtain a better insight into the effect of extended germination as this species is used more frequently in malting. Sprouted seeds were separated and kiln-dried at 50 °C in an air oven and the rootlets were removed by gentle brushing. Devegetated seeds were weighed and powdered in a plate mill (60 BS mesh). Native millet meals were used as control samples. Starch contents of the samples were estimated by enzymatic hydrolysis (Chiang & Johnson, 1977).

### Isolation of free sugars and non-starchy polysaccharides

Defatted (with hexane) millet meals were suspended in an excess of aqueous ethanol (70%), refluxed for about 6 h and centrifuged. Free sugars from the extract and non-starchy polysaccharides from the residues were isolated according to the methods described by Salimath & Tharanathan (1982).

Total sugars, pentosans, uronic acid and protein content of the isolates were estimated by phenol–sulphuric acid (McKelvy & Lee, 1969), phloroglucinol (Douglas, 1981), carbazole (Knutson & Jeanes, 1968) and micro-Kjeldahl procedures, respectively, and the total hexose content was calculated from the difference between total sugar and pentose plus uronic acid values.

The polysaccharide samples were hydrolysed with 2N sulphuric acid at about 100°C for 12 h, neutralised with solid barium carbonate, concentrated under reduced pressure and used for qualitative and quantitative analysis of sugars by paper and gas–liquid chromatography (Salimath & Tharanathan, 1980). For descending paper chromatography, Whatman No. 3 filter paper sheets irrigated with *n*-propanol–ethanol–water (7:1:2 v/v) were used. The spots were developed with aniline-phthalate (Partridge, 1969) or urea–HCl (Dedonder, 1952) spray reagents. Individual sugars were eluted with water and estimated (McKelvy & Lee, 1969). For gas–liquid chromatography, a gas chromatograph (Varian model 3700) fitted with a flame ionisation detector and a stainless steel column packed with 3% ECNSS-M on Gas Chrom Q (100–120 mesh) was used. The column temperature was maintained at 170°C and nitrogen (15 ml/min) was the carrier gas. Alditol acetate derivatives were prepared according to the method of Sawardeker *et al.* (1965).

## RESULTS AND DISCUSSION

From the results presented in Table 1, it is apparent that the recovery of ethanol-soluble sugars, reflected in the higher contents of glucose, fructose and maltose, is higher in malted millets than in the unmalted samples. Finger millet samples germinated for 96 h contained 9-, 7- and 60-fold higher glucose, fructose and maltose, respectively, than those of native millet. However, the content of sucrose in all samples remained fairly constant on malting. Small amounts of raffinose found in ungerminated finger millet disappeared on germination, probably due to an enhanced galactosidase activity.

The yield and composition of various non-starchy polysaccharides of native and malted millets are presented in Table 2. A significant increase in the water-soluble non-starchy polysaccharides (WSNSP), a slight decrease in hemicellulose-A but a marked increase in cellulose-type fractions were observed in malted millets. The WSNSP fractions from native millets contained higher proportions of pentoses than hexoses but malted millets contained more hexoses than pentoses. The WSNSP fractions contained about 10% pectic substances measured as galacturonic acid, whereas the other polysaccharide fractions contained only small amounts of pectic materials. All fractions contained protein, as was also observed by Emiola & De La Rosa (1981) in the case of pearl millet.

**TABLE 1**

Composition of Aqueous Ethanol (70%) Extractable Sugars, Starch Content and Yield of Native Millets and Their Malts (g/100 g sample)

| *Sample* | *Glucose* | *Fructose* | *Maltose* | *Sucrose* | *Raffinose* | *Stachyose* | *Total* | *Starch* | *Yield of malt* |
|---|---|---|---|---|---|---|---|---|---|
| $R_0$ | 0·19 | 0·14 | 0·04 | 0·66 | 0·01 | — | 1·04 | 65·5 | 100 |
| $R_2$ | 0·82 | 0·61 | 1·05 | 0·64 | — | — | 3·12 | 57·9 | 87·2 |
| $R_4$ | 1·65 | 0·94 | 2·38 | 0·95 | — | — | 5·92 | 53·0 | 69·1 |
| $B_0$ | 0·18 | 0·17 | 0·08 | 0·79 | 0·14 | 0·08 | 1·44 | 69·0 | 100 |
| $B_2$ | 1·17 | 0·98 | 1·28 | 0·62 | — | — | 4·05 | 61·4 | 91·2 |
| $N_0$ | 0·12 | 0·11 | 0·06 | 0·70 | 0·05 | — | 1·04 | 60·3 | 100 |
| $N_2$ | 0·73 | 0·55 | 0·89 | 0·64 | — | — | 2·81 | 55·8 | 90·4 |

Values expressed on a dry weight basis of devegetated malt.
Average of two determinations reported.
$R_0$, $R_2$ and $R_4$ represent native, 48 h and 96 h germinated finger millet, respectively.
$B_0$ and $B_2$ represent native and 48 h germinated pearl millet, respectively.
$N_0$ and $N_2$ represent native and 48 h germinated foxtail millet, respectively.

**TABLE 2**

Yield (%) and Composition of Non-Starchy Polysaccharides of Native and Malted Millets

| Sample[a] | WSNSP | | | | Hemicellulose-A | | | | Hemicellulose-B | | | | Cellulose-type | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Yield | Pentoses | Hexoses | Uronic acid | Yield | Pentoses | Hexoses | Uronic acid | Yield | Pentoses | Hexoses | Uronic acid | Yield | Pentoses | Hexoses | Uronic acid |
| $R_0$ | 1·05 | 63·5 | 27·1 | 9·4 | 2·3 | 60·2 | 36·8 | 3·0 | 2·7 | 64·0 | 33·1 | 2·3 | 6·1 | 26·1 | 72·1 | 1·8 |
| $R_2$ | 1·34 | 53·4 | 35·4 | 11·2 | 2·0 | 81·4 | 16·3 | 2·3 | 2·6 | 63·4 | 34·6 | 2·0 | 7·2 | 28·3 | 69·8 | 1·9 |
| $R_4$ | 1·62 | 35·0 | 51·9 | 13·1 | 1·9 | 89·5 | 6·3 | 4·2 | 2·8 | 64·0 | 34·2 | 1·8 | 8·4 | 30·1 | 68·1 | 1·8 |
| $B_0$ | 1·24 | 64·7 | 22·7 | 12·6 | 2·6 | 47·7 | 47·0 | 5·3 | 3·0 | 60·3 | 36·9 | 2·8 | 4·0 | 22·5 | 66·0 | 1·5 |
| $B_2$ | 1·39 | 49·3 | 36·7 | 14·0 | 2·4 | 68·2 | 26·0 | 5·8 | 2·8 | 60·3 | 37·1 | 2·6 | 4·7 | 24·2 | 74·3 | 1·5 |
| $N_0$ | 0·90 | 55·4 | 33·0 | 11·6 | 2·2 | 43·2 | 52·5 | 4·3 | 2·3 | 72·0 | 26·4 | 1·6 | 10·4 | 18·7 | 79·6 | 1·7 |
| $N_2$ | 1·02 | 44·0 | 42·7 | 13·3 | 2·1 | 58·4 | 37·1 | 4·5 | 2·1 | 70·0 | 28·4 | 1·6 | 11·5 | 20·3 | 78·1 | 1·6 |

[a] For details, see Table 1.

Values expressed on a dry weight basis. Average of two determinations reported.

Percentages of pentose, hexose and uronic acid calculated on the basis of total carbohydrates.

**TABLE 3**

Relative Proportion (%) of Constituent Sugars of Non-Starchy Polysaccharides Present in Native ($R_0$), 48 h ($R_2$) and 96 h ($R_4$) Malted Finger Millet Samples

| *Fractions* | *Sample*[a] | *Arabinose* | *Xylose* | *Glucose* | *Galactose* | *Mannose* | *Rhamnose* |
|---|---|---|---|---|---|---|---|
| Water soluble | $R_0$ | 35·5 | 35·5 | 4·5 | 7·3 | 7·8 | 9·4 |
| | $R_2$ | 28·9 | 28·9 | 17·2 | 7·2 | 8·2 | 9·6 |
| | $R_4$ | 20·9 | 20·9 | 34·8 | 7·0 | 6·6 | 9·8 |
| Hemicellulose-A | $R_0$ | 32·7 | 30·7 | 34·4 | 0·6 | Trace | 1·6 |
| | $R_2$ | 43·4 | 43·0 | 11·3 | 1·3 | Trace | 1·0 |
| | $R_4$ | 48·1 | 42·4 | 2·7 | 2·5 | Trace | 4·3 |
| Hemicellulose-B | $R_0$ | 35·2 | 35·2 | 24·4 | Trace | — | 5·2 |
| | $R_2$ | 35·1 | 35·1 | 24·3 | Trace | — | 5·5 |
| | $R_4$ | 33·7 | 33·7 | 27·9 | Trace | — | 4·7 |
| Cellulose-type | $R_0$ | 14·1 | 14·3 | 65·9 | Trace | — | 5·7 |
| | $R_2$ | 22·2 | 15·2 | 59·6 | Trace | — | 3·0 |
| | $R_4$ | 21·5 | 17·1 | 59·2 | 0·5 | — | 1·7 |

[a] For details, see Table 1.

From Table 3 it may be seen that pentoses (arabinose and xylose) were the major sugar components in the WSNSP fraction of native finger millet but that the concentration of glucose was considerably higher in malt samples. Small amounts of galactose, mannose and rhamnose were also present and, quantitatively, these sugars remained at the same level after malting. As expected, the hemicellulose-A fraction also contained a higher proportion of pentoses and their concentration increased on malting. The sugar composition of the hemicellulose-B fraction changed little on malting. Although glucose was the predominant sugar in the cellulose-type fraction, it still contained considerable amounts of arabinose and xylose. The latter may probably be due to the incomplete extraction of hemicellulose(s).

The increase in free sugar content after malting is mostly at the expense of hydrolysed starch and the pattern of changes in free sugars observed in millets after malting is generally similar to that reported for other cereals (Briggs *et al.*, 1981; Munck *et al.*, 1981; Glennie *et al.*, 1983). The increase in reducing sugars, especially in maltose content, has been observed in pearl millet (Opoku *et al.*, 1983) and sorghum (Aisien, 1982). The variation in the content and composition of non-starchy polysaccharides is due to the depletion of embryo and starchy endosperm to meet the requirement of seedlings, and also may be due to the synthesis of new cell wall materials. This was evidenced by the lowering of the yield of devegetated malt on malting (Table 1). This could explain the slight increase in the cellulose-type material after malting observed in all millets. In the case of barley, it has been reported that the NSP of endosperm undergo more structural changes than the seed coat material (Woolard *et al.*, 1977).

From this study it may be deduced that germination or malting of millets enhances the contents of low molecular weight sugars. However, the slight increase in the content of NSP may not be desirable and could possibly be reduced by debranning the malted seeds (Malleshi & Desikachar, 1981).

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