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# Free sugars and non-starch polysaccharide contents of good and poor malting varieties of wheat and their malts

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The yield and composition of low molecular weight sugars and non-starch polysaccharides (NSP) of a good- and a poor-malting variety of wheat and their malts were determined. There were seven, four and six-fold increases in total sugars, sucrose and maltose, respectively, on 120 h germination in both varieties, the increase being higher in the good-malting variety than in the poor-malting variety. The poor-malting variety contained slightly (11.7%) higher levels of total NSP than the good-malting variety (10.9%). The uronic acid formed 2.5 to 23.3% of the different NSP fractions, the highest being in EDTA-extractable (EDTAE) fractions. The hexose content of the cold water-soluble fraction decreased from 63.4 to 20% on malting in the good-malting variety but its content remained the same in the poor-malting variety. Mannose was detected only in the EDTAE fraction of the good-malting variety and its concentration decreased from 24.2 to 4.6% on malting. Malt samples from both varieties contained slightly higher levels of hemicellulose A, hemicellulose B and cellulosic fractions, and lower levels of EDTAE NSP fractions. The water-soluble fraction was 45% of the total NSP of the good-malting variety and 28% of the poor-malting variety. © 1997 Elsevier Science Ltd

## INTRODUCTION

Malting of wheat is gaining prominence for food (Livingstone *et al.*, 1993), beverages (Javalagi & Vaidehi, 1986) and also as an extender to barley in brewing (Briggs & Wadeson, 1986). Varietal variation with respect to malting of wheat is also reported (Pomeranz *et al.*, 1975; Singh *et al.*, 1983). Non-starch polysaccharides (NSP) form the major components of seed coat, cell walls and also the cell-binding materials in the endosperm of cereals. The NSP constituents hinder the easy migration of the hydrolytic enzymes during germination and affect the malt modification (Lineback & Rasper, 1988). The free sugars of the seed form the source of energy for the biochemical activities during the initial stages of germination and also contribute to the malting quality. During germination, a considerable increase in the free sugars content occurs due to partial hydrolysis of starch but, simultaneously, some of the free sugars are utilised for the metabolic activity; as a result, their concentration in the malt largely depends on the malting quality of the seed material. The free sugars and the non-starch polysaccharides (dietary fibre components) also influence the food quality of malt. Information about the content and composition of NSP fractions of wheat varieties of varying malting quality may help in understanding the role played by these seed constituents on malting of wheat and also in breeding malt wheat. The contents and composition of free sugars and NSP of good- and poor-malting wheat varieties and their malts are reported in this paper.

## MATERIALS AND METHODS

Two varieties of wheat identified as a good-(HD 2189) and a poor-(D 651) malting strain (Suhasini, 1994), obtained from the University of Agricultural Sciences, Dharwad, India, were used for the studies. Seeds were steeped in water for 16 h and germinated on moist cloth at 25°C in a BOD incubator. The seeds germinated up to 72 and 120 h were collected separately, dried at 50°C in an air-oven to about 10% moisture and the vegetative portion removed by gentle brushing. The native wheat

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and the devegetated seeds were pulverized in a Udy cyclone sample mill (Udy Corporation, Colorado, USA) fitted with 0.5 mm screen and the whole meals were defatted with petroleum ether. Free sugars were isolated from native, 72- and 120-h malted samples, whereas NSP were isolated from native and 72-h malted samples only.

### Isolation of free sugars and NSP

The free sugars from the samples were extracted with 70% aqueous ethanol and, from the residue the non-starch polysaccharide (NSP) fractions, viz., cold water-soluble NSP (CWSNSP) hot water-soluble NSP (HWSNSP), EDTA extractables (EDTAE), hemicellulose A (HA), hemicellulose B (HB) and cellulosic fractions CF) were extracted sequentially. The isolation and purification of the free sugars and the NSP fractions were carried out following the method of Paramahans and Tharanathan (1982).

### Characterization of free sugars

The aqueous ethanol extracts were treated on Dowex resins, concentrated and filtered through a millipore filter and the total sugar content of the filtrate was determined (Dubois *et al.*, 1956). The component sugars were resolved and identified by high performance liquid chromatography (C-R4 A, Shimadzu) using a micro-bonda pack amino column (4.1 mm×30 cm) and eluted with an acetonitrile and water (80:20) solvent system at a flow rate of 1 ml $min^{-1}$ (McGinnis & Fang, 1980). Glucose, fructose, galactose, maltose, sucrose, raffinose and stachyose were the reference sugars. The area under each peak was measured to quantify individual sugars. Under the experimental conditions 'glucose and fructose' and 'sucrose and maltose' were eluted together due to their close retention times. Hence, glucose was estimated by glucose oxidase method (Dahlqvist, 1964) and, separately, sucrose by the AACC (1983) method.

### Characterization of NSP

The isolated NSP fractions (10 mg) were suspended in water (0.5 ml) and solublised in concentrated $H_2SO_4$ (0.6 ml) at ice cold temperature, after which the concentration of $H_2SO_4$ was lowered to 8% by addition of water, refluxed in a water bath for 10 to 12 h and the volume made up to 20 ml. Total sugars and uronic acid contents of the hydrolysates were estimated according to the methods of Dubois *et al.* (1956) and Knutson and Jeanes (1968), respectively. Alditol acetate derivatives of the NSP fractions were prepared following the method of Sawardekar *et al.*, (1965) and the component sugars were separated and identified on a 3% OV-225 (1/8″× 6′) column using a Packard gas chromatograph (model 427) equipped with flame ionization detector at 190°C column temperature and 230°C injector and detector port temperatures. Nitrogen (15 ml $min^{-1}$) was used as the carrier gas. A sugar mixture consisting of rhamnose, fucose, arabinose, xylose, mannose, galactose and glucose was used as reference sugars and inositol as the internal standard.

## RESULTS AND DISCUSSION

### Free sugars

The component sugars detected in aqueous ethanol from the native and malted wheat were glucose, fructose, sucrose, maltose and raffinose. The total free sugar content was higher in the good-malting variety than in the poor-malting variety (Table 1). There was a six-fold increase in the total free sugar content on germination in both varieties, the increase being about thirty-fold in glucose, fifteen-fold in fructose, six-fold in maltose and three-fold in sucrose on 120 h of germination. Traces of raffinose were detected in native samples but not in malt. The increase in sugars is attributed to the hydrolysis of starch by amylases during germination (Kruger, 1989), and the increase in sucrose could be due to hydrolysis of oligosaccharides of the raffinose series. The increases in free sugars and loss of raffinose on germination of cereals have also been reported in wheat (Kruger & Matsuo, 1982), barley (Woolard *et al.*, 1977), sorghum (Aisien, 1982) and millets (Malleshi *et al.*, 1986).

### Non-starchy polysaccharides

The yield and composition of various non-starch polysaccharides (NSP) of both the good-(HD 2189) and the poor-(D 651) malting varieties from their native and malted wheat are presented in Table 2. The total NSP content of HD 2189 variety (10.9%) was slightly lower than that of D 651 variety (11.7%); however, the total NSP contents of malt samples of both varieties were much higher than the respective native samples. The cold water-soluble NSP (CWSNSP) constituted nearly 30% of the total NSP of native HD 2189 as well as D 651 varieties and its content remained unaltered in the former but decreased by 19% in the latter on malting. The hot water-soluble NSP (HWSNSP) fraction content

**Table 1. Yield and composition of aqeous ethanol-extractable sugars of native and malted wheat varieties (g 100 $g^{-1}$)**

| Sample | Glucose | Fructose | Sucrose | Maltose | Rafinose | Total |
|---|---|---|---|---|---|---|
| HD 2189 variety | | | | | | |
| Native | 0.05 | 0.07 | 0.50 | 0.66 | 0.04 | 1.32 |
| 72 h | 0.98 | 0.86 | 0.70 | 2.31 | 0.01 | 4.86 |
| 120 h | 1.90 | 1.40 | 1.70 | 3.70 | Nil | 8.70 |
| D 651 variety | | | | | | |
| Native | 0.04 | 0.07 | 0.30 | 0.48 | 0.03 | 0.92 |
| 72 h | 0.56 | 0.40 | 0.80 | 1.50 | Nil | 3.26 |
| 120 h | 1.20 | 0.99 | 1.30 | 2.83 | Nil | 6.32 |

**Table 2. Yield and composition (realative percentage of sugars) of non-starch polysaccharides of native and malted wheat varieties**

| | | Cold water-solubles | | Hot water-solubles | | EDTA extractables | | Hemicellulose-A | | Hemicellulose-B | | Cellulose | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | HD 2189 | D 651 | HD 2189 | D 651 | HD 2189 | D 651 | HD 2189 | D 651 | HD 2189 | D 651 | HD 2189 | D 651 |
| Yield, % | N | 3.05 | 2.48 | 1.88 | 0.83 | 0.46 | 0.27 | 0.35 | 1.10 | 1.95 | 3.09 | 3.21 | 3.89 |
| | M | 3.89 | 2.43 | 1.54 | 0.74 | 0.19 | 0.18 | 0.55 | 1.15 | 2.68 | 3.71 | 4.05 | 4.62 |
| Uronic acid | N | 9.6 | 11.9 | 14.5 | 9.2 | 18.5 | 21.3 | 7.4 | 5.0 | 4.2 | 4.2 | 2.9 | 3.3 |
| | M | 8.6 | 13.4 | 11.0 | 10.0 | 13.1 | 23.3 | 7.1 | 4.1 | 4.1 | 3.9 | 2.5 | 3.0 |
| Arabinose* | N | 15.5 | 16.6 | 60.7 | 53.3 | 20.5 | 43.9 | 16.9 | 18.7 | 56.6 | 42.0 | 21.7 | 23.0 |
| | M | 41.0 | 21.6 | 51.4 | 49.0 | 35.7 | 48.3 | 22.8 | 16.4 | 40.3 | 47.3 | 23.2 | 23.0 |
| Xylose* | N | 19.5 | 23.5 | 39.3 | 46.7 | 21.3 | 50.9 | 44.4 | 58.4 | 37.7 | 47.7 | 19.0 | 17.9 |
| | M | 38.6 | 16.4 | 48.6 | 51.0 | 45.5 | 51.7 | 53.9 | 65.7 | 51.7 | 52.7 | 18.4 | 17.9 |
| Mannose* | N | — | — | — | — | 24.2 | — | — | — | — | — | — | — |
| | M | — | — | — | — | 4.6 | — | — | — | — | — | — | — |
| Galactose* | N | — | — | — | — | 3.5 | 5.2 | — | — | — | — | — | — |
| | M | 4.9 | — | — | — | 1.9 | — | — | — | — | — | — | — |
| Glucose* | N | 65.3 | 59.9 | — | — | 30.5 | — | 38.7 | 22.9 | 5.8 | 10.4 | 59.3 | 59.1 |
| | M | 15.5 | 62.0 | — | — | 12.3 | — | 23.2 | 17.8 | 8.0 | — | 58.4 | 59.1 |
| Pentoses | N | 34.7 | 40.1 | 100.0 | 100.0 | 41.8 | 94.8 | 61.3 | 77.1 | 94.3 | 89.7 | 40.7 | 40.9 |
| | M | 79.6 | 38.0 | 100.0 | 100.0 | 81.2 | 100.0 | 76.7 | 82.2 | 92.0 | 100.0 | 41.6 | 40.9 |
| Hexoses | N | 65.3 | 59.6 | — | — | 58.2 | 5.2 | 38.7 | 22.9 | 5.8 | 10.4 | 59.3 | 59.1 |
| | M | 20.4 | 62.0 | — | — | 18.8 | — | 23.3 | 17.8 | 8.0 | — | 58.4 | 59.1 |

N. Native wheat; M. 72 h malted wheat * Proportion based on 100% carbohydrates

was considerably higher in D 651 than in HD 2189. The poor-malting variety also contained higher levels of hemicellulose B (HB) fraction as compared to the good-malting variety. The cellulosic fraction (CF) accounted for 30% of NSP in both varieties. Malting enhanced CWSNSP, HA, HB and CF and lowered EDTAE and HWSNSP fractions in both varieties. The loss of some starch on malting may be the major contributing factor to the increase in NSP component of the seed.

Glucose was the major constituent sugar of the CWSNP of the native wheat. On malting, the glucose content of HD 2189 decreased whereas no appreciable change of its content in D 651 was observed. This may perhaps be due to higher levels of β-D-glucanase developed in the good-malting variety, which might have solublized and liberated the β-D-glucose. Arabinose and xylose were the only sugars present in HWSNSP of native and malted wheat. The yield and the hexose content of the EDTAE fraction decreased on malting in both varieties. Arabinose, xylose, glucose, mannose and galactose were detected in the EDTAE fraction of native HD 2189, but only arabinose, xylose and galactose were detected in the native D 651 variety.

The hemicellulose A fraction constituted 3.5 and 2.5% of the total NSP in the native HD 2189 and D 651 varieties, respectively, and there was not much change in its yield on malting. However, on malting there was a reduction in glucose content of this fraction in both varieties which could be due to the enhanced activity of β-D-glucanase (Kruger & Reed, 1988). Although glucose was the main constituent sugar of the cellulose fraction, it contained an appreciable quantity of pentoses. Malleshi *et al.* 1986) also observed considerable amounts of arabinose and xylose in the cellulosic fraction of millets and attributed this to incomplete extraction of hemicelluloses.

The values for the total NSP content of the native samples in the present studies are in agreement with those reported for whole wheat flour (10.15%) by Englyst *et al.* (1983). The higher levels of total NSP in D 651 (poor-malting variety) might have contributed to the rigid structure of the cell walls, thereby obstructing the easy entry of enzymes into the endosperm resulting in poor malt modification. It may be worthwhile to note that the total water-soluble fractions (WSNSP) comprised about 47% of NSP in the good-malting strain compared to 29% in the poor-malting strain. On the other hand, the good-malting wheat contained less CF than the poor-malting strain. It is possible that part of the WSNSP would have leached out during steeping and facilitated easy movement of enzymes during germination.

The studies indicated that the free sugar contents increased appreciably on malting of wheat and the increase was higher in a good-malting variety than in a poor-malting variety. The total non-starch polysaccharide content was slightly higher in the poor-malting variety than the good-malting variety; the latter contained higher levels of water-soluble NSP than the former. It may be inferred that soluble NSP can be taken as one of the good indicators for determining the malting quality of wheat.

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