Extraction, structure and functional properties of maize bran heteroxylans

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Extraction, Structure and Functional Properties of Maize Bran Heteroxylans

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Heteroxylans are cell wall polysaccharides representing ~50% of maize bran. They are easily extracted in hot alkaline conditions, giving a water-soluble polysaccharide. Temperature and alkali concentration are the main parameters affecting the extraction yields. Yields of 90% were obtained with KOH 1.5M at 100°C for 2h. The extracted heteroxylans had constant composition and contained Ara:Xyl:Gal:GlcA (molar ratio 1:1.7:0.2:0.2). Intrinsic viscosity [η] was about 180 ml/g and weight average molecular weight (M_w) about 290 000 g/mol. The composition, structure and physico-chemical properties of the polysaccharides were stable whatever the extraction conditions used.

Heteroxylans were very soluble in cold water and solutions up to 20% (w/v) were easily obtained. Solutions of heteroxylans exhibited Newtonian behaviour even at high concentration, and their viscosities were in between the viscosities of arabic and ghatti gum solutions. Heteroxylans exhibited marked emulsion stabilizing property. Films of heteroxylans were easily made. Their mechanical properties were dependent on the plasticizer and water amount but were comparable to those of other hydrophilic film-forming biopolymers. Their gas barrier properties to O_2 and CO_2 were interesting compared to other biopolymer-based films.

Maize brans (hulls) are by-products of the semolina industry of low value mainly used for animal feeding. Each year about 70 000 tons of brans are produced. About 50% of the bran are constituted by heteroxylans, which are cell-wall polysaccharides. Cosmetics, pharmaceutical as well as food industries are always looking for new hydrocolloids of stable functional properties at the best price. We present here some results on the alkaline extraction and functional properties of maize bran heteroxylans which demonstrate their possible use as ingredients in food and non-food applications.

Results and Discussion

Chemical Composition

Maize bran contained about 50% (w/w) of heteroxylan[1] as calculated as the sum of xylose (28.4%) arabinose (16.2%) galactose (5%) and glucuronic acid (4.2%). Remaining material was mainly cellulose (20%), phenolic acids (mainly ferulic acid and its dimers), acetic acid and proteins representing each about 5% of the bran. Traces of lignin were also detected (<1%).

Extraction and characterization of heteroxylans

Response surface methodology was used to study the alkaline extraction of heteroxylans from maize bran[2]. The ratio volume of alkali/weight of bran, and the particle size had no effect on extraction yield, whereas the yield increased significantly with the temperature and time of extraction and the concentration of the alkali. The variation of the yield depended on the nature of the alkali. Empirical second order model for KOH extraction is shown on Fig.1. KOH extraction was not time dependent within the initial period of 1h and a fixed time of extraction, 2h, was used to establish the model.

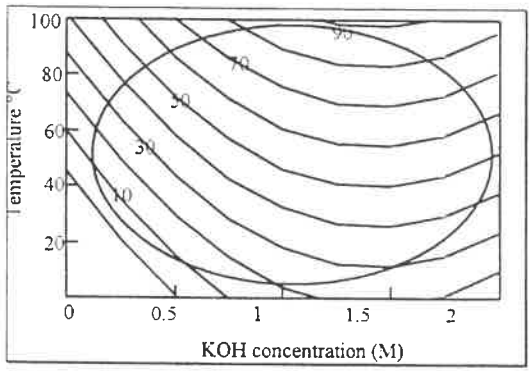

Figure 1. Response-surface diagram of arabinoxylan extraction yield as a function of KOH concentration and extraction temperature. Solid lines indicate the yield iso-curves; the dotted oval line delimits the model's validity domain.

Heteroxylan extraction was fast and easy and very high yields were obtained.

Table I. Composition (%,w/w, dry-weight basis) extracted heteroxylans

	Extraction	Yield	Ara	Xyl	Gal	GlcA	Glc	Protein
HX1	KOH 1.5M 95°C	92%	28.5	47.1	7.5	5.8	1.0	4.5
HX2	$Ca(OH)_2$ 95°C	64%	27.9	48.1	7.2	6.6	1.1	2.5
HX3	KOH 0.5M 65°C	59%	27.2	45.7	7.1	6.9	0.5	4.3

In order to check wether or not the different extraction conditions influenced the nature and the structure of extracted polysaccharides, 3 different extractions were used (Table I) with hard (HX1) to mild conditions (HX3).

Whatever the conditions used, the composition of the extracted polysaccharides was similar (Table I) as well as their intrinsic viscosities (186, 175 and 171 ml/g, for HX1, HX2 and HX3, respectively). All the heteroxylans exhibited a polyelectrolyte character[3] due to the presence of glucuronic acid and their weight average molecular weight as determined by light scattering methods were very similar (310 000, 280 000 and 270 000 g/mol for HX1, HX2 and HX3, respectively)[4]. Polydispersity index, the ratio of M_w/M_n, was found to be around 24.

The structure of the heteroxylans was unchanged by the different extraction conditions[1,2,5]. The structure was typical of highly branched heteroxylans with approx. 80% of the xylose residues in the β(1→4)-linked backbone bearing side-chains. These branches were located on O-2 or/and O-3 of the xylan backbone and were mainly composed of single arabinose residues, but longer chains of 2-3 sugar residues (containing arabinose, xylose and galactose) were also present[6]. Single glucuronic acid residue was also a side-chain component .

Finally, extracted heteroxylans exhibited high purity and chemical homogeneity, and their composition and structure were independent of extraction conditions suggesting a high stability of their functional properties.

Functional properties

The intrinsic viscosities ([η]) of heteroxylans were found around 180 ml/g, which indicates rather moderate thickening properties in dilute solutions. Their behaviour was studied for concentrated solutions (Fig.2).

HX1 exhibited Newtonian behaviour even in concentrated solutions, whereas a

shear thinning behaviour was observed for the most concentrated solutions of HX3 (>100 mg/ml). The near Newtonian behaviour of heteroxylan solutions, different to the shear thinning behaviour of most hydrocolloids, leads to different mouthfeeling characteristics.

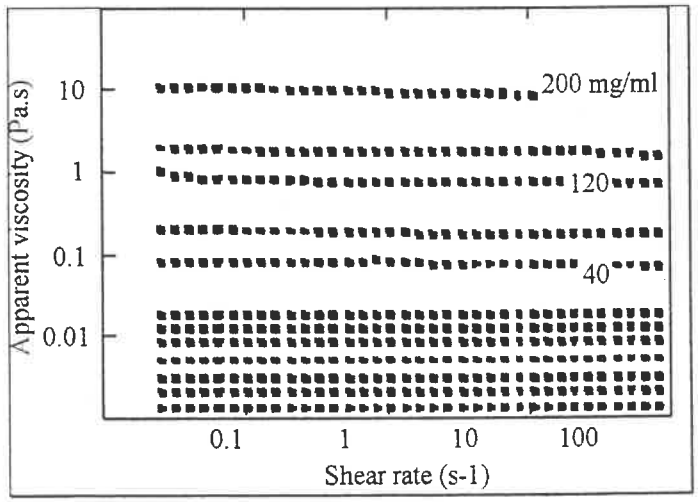

Figure 2. Effect of shear rate on the apparent viscosity of HX1 solutions. From the bottom to the top: 3 to 200 mg/ml.

Maize bran heteroxylan thickening properties were compared with those of commercial shear thinning hydrocolloids (Fig.3).

For all concentrations, viscosimetric behaviour of HX1 and HX3 samples was close and the heteroxylan viscosity was found intermediate between those of arabic and ghatti gums, both weak thickener. Viscosities of maize bran heteroxylans were previously found intermediate between karaya and arabic gums[7]. All these results indicate that heteroxylans from maize bran had moderate thickening properties similar to those of exudate gums.

Emulsifying properties of heteroxylans were studied, and flocculation-creaming kinetics are shown in Fig 4.

The variations of the initial flocculation rate had identical shape for HX3 and arabic gum, but for the same concentration, HX3 rate was always smaller than the one

of arabic gum and got nil for 20 mg/ml of heteroxylans in aqueous phase. In the same way, the volumic fraction of the equilibrium separated aqueous phase was higher for arabic gum than for HX3. These differences were partly due to the aqueous phase viscosity which, at the same concentration, was higher for heteroxylan than for arabic gum. The stability of the emulsions towards coalescence was also studied by centrifugation. Complete stabilization of the emulsion was obtained for concentrations of 2.3 mg/ml with HX3 and 8.3 mg/ml with arabic gum, which means that an interfacial film appeared for a smaller concentration of heteroxylans than for the sample of arabic gum we have used. However this concentration was much higher than the concentration of proteins required for stabilization (0.2mg/ml for BSA). This adsorption ability of maize bran heteroxylans might be due to their protein fractions[2].

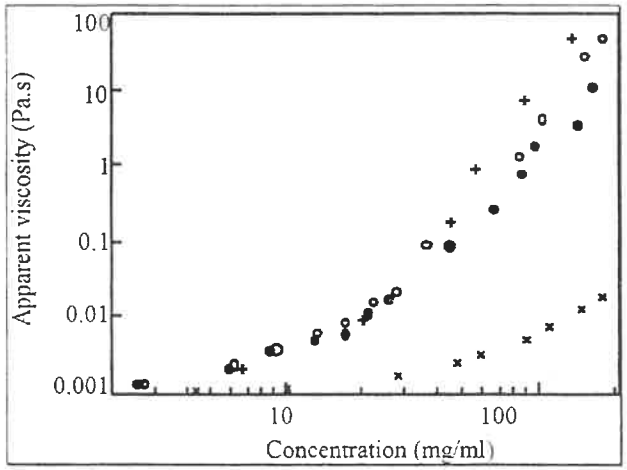

Figure 3. Apparent viscostity (measured at 5 s^{-1} shear rate) versus concentration of maize bran heteroxylans (HX1 : ● ; HX3: ○), arabic (x) and ghatti (+) gum.

Filmogenic properties of HX were also studied. The mechanical properties of heteroxylan films were dependent on the nature and the proportion of plasticizer added as well as the relative humidity which modified the water content of the film. The most effective plasticizer was glycerol and its effects are shown on Fig.5.

Tensile strength decreased (from 25 to 1 MPa) as concentration of glycerol increased, while elongation (from 2 to 70 %) and stickiness increased. These values were in the same rank than those of the other film-forming biopolymers (Starch, gluten).

Barrier properties were tested on films with 15 % glycerol. The water vapor permeability was rather high ($9.76x10^{-11}\pm0.40x10^{-11}$ g.m.m^{-2}.s^{-1}.Pa^{-1}) as expected for an hydrophilic film. The oxygen permeability was $0.15x10^{-11}\pm0.02x10^{-11}$ g.m.m^{-2}.s^{-1}.Pa^{-1} and the carbone dioxyde permeability was $0.23x10^{-11}\pm0.02x10^{-11}$ g.m.m^{-2}.s^{-1}.Pa^{-1}. These two values were rather low compared to those of other film-forming biopolymers e.g. gluten (O_2 and CO_2 permeability = 0.2 and 0.4 g.m.m^{-2}.s^{-1}.Pa^{-1}, respectively).

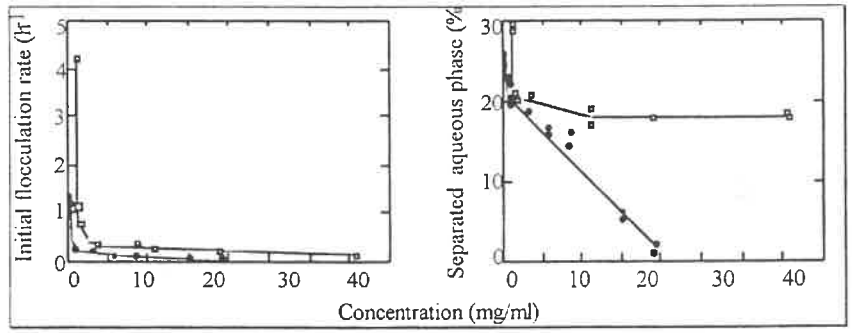

Figure 4. Initial flocculation rate and equilibrium separated aqueous phase as a function of polysaccharide concentration; ❑ : arabic gum , ● : HX3.

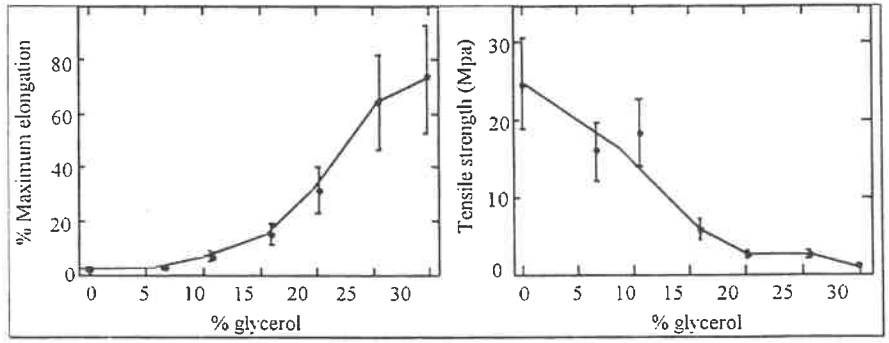

Figure 5. Effect of glycerol on tensile strength and elongation of heteroxylan films.

Conclusion

Heteroxylans are very easily extracted from the bran by alkaline treatment and exhibit homogeneous and stable structure whatever the conditions of extraction used. These features allow to obtain stable functional properties which is rarely observed for natural hydrocolloïds and of a great importance in industrial processes. The high solubility, moderate viscosity, odourless and tasteless of heteroxylans suggest that they might be used as stabilizing and texturizing agents in cosmetic and pharmaceutical industry. Owing to their emulsifying and filmogenic properties, they also have potential uses as surface finishing agent (paper), flavouring agent (encapsulation) and adhesive agent. Actually, heteroxylans properties match with some of arabic gum properties which is widely used in food and non-food applications.

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Physicochemical Modifications of Inulin: Properties and Applications

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Inulin is a polydisperse mixture consisting mainly of linear chains of β(2→1) linked D-fructofuranose units with an α-D-glucopyranose unit at the reducing end. It is a plant polysaccharide and the average degree of polymerisation varies from 5-30 depending on the plant from which it originates. Inulin is produced on an industrial scale mainly from chicory roots and is currently used as a dietary fiber and as texturizing ingredient in food.

Inulin and most inulin-derivatives are biodegradable. Due to their structural features these compounds display interesting physical properties which differentiate them from other industrial biopolymers. These characteristics, like good water solubility, low viscosity and high potential degree of substitution, make them attractive candidates in non-food applications, especially in markets with a demand for environmentally friendly biodegradable alternatives for petrochemicals. Examples are the inulin based polycarboxylates such as dicarboxyinulin (DCI) and carboxymethylinulin (CMI). DCI shows excellent Ca-sequestering properties and good $CaCO_3$-dispersing properties, whereas CMI shows good crystal growth inhibition. These compounds may find possible applications as a replacement for poly-acrylates in detergents, and in products for industrial cleaning, water treatment (scale inhibitor) and textile treatment.

Furthermore, some recent developments on the synthesis of sulfur containing inulin derivatives with possible applications in heavy-metal removal from waste-materials will be discribed. Finally the possible use of inulin as an ingredient for adhesives will be discussed.

Inulin is a reserve plant polysaccharide occurring in the roots and tubers of plants which belong to the families of the *Liliaceae* and the *Compositae*. The most important sources for production of inulin are Jerusalem artichoke, Dahlia and Chicory which have a high inulin content (> 10% based on fresh weight, Tab.I). Currently the main source for industrial production of inulin is chicory roots. The three major producers in Western Europe are Sensus, a business unit of Coöperatie Cosun U.A., Orafti and Warcoing.

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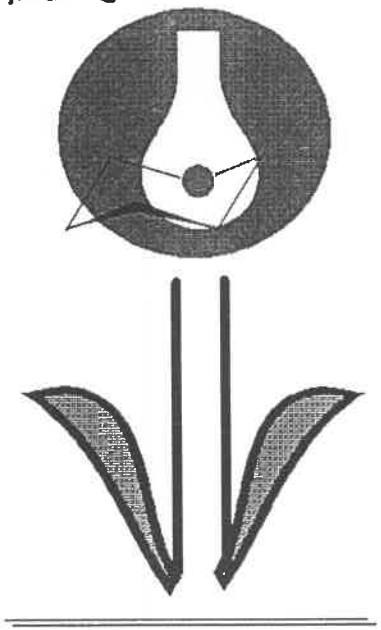

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