Direct conversion of wheat bran hemicelluloses into n-decyl-pentosides†

Sinisa Marinkovic and Boris Estrine*

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Direct preparation of pentose based surfactants has been achieved by a direct conversion of wheat bran hemicelluloses in decanol under smooth conditions. Hemicelluloses have been efficiently converted in a single step operation. The wheat-based surfactants thus obtained have shown good surface properties compared to other alkyl glycosides. In view of the growing importance of renewable resource based molecules in detergents and cosmetics industries, this approach may open a new avenue for the production of green surfactants.

1. Introduction

Hemicellulose, the second most abundant source of biomass next to cellulose, is currently regarded as a promising alternative for fossil chemicals as it cannot be digested by human beings and thus its use, unlike corn and starch, will not impose a negative impact on food supplies. Wheat bran represents a valuable source of hemicellulose; it is an available co-product of wheat that has strong potential tonnages. In a context where interest is constantly growing for integrated lignocellulosic biorefineries, there is a need to better use the hemicellulose part of crops and to improve the added-value of such concepts.[1] The selection of ingredients for use in detergents usually depends on the nature and compatibility of the various chemicals being formulated, the application, and economics. The actual regulatory context is now drawing formulators' attention to new chemicals that are well balanced between efficiency and environmental impacts. Although today some green surfactant solutions are available, most of them are based on food related sugars like glucose and stay poorly used due to their price. It is the case for alkyl polyglucosides (APG). APG are non-ionic surfactants produced from fatty alcohols from vegetable oils and glucose from starch, and have become important as complements to ethoxylates and have good impact on the environmental profile of detergent. Works have been published recently where some direct conversion routes from cellulose to alkyl glucosides were reported. In these studies, some drastic conditions are applied, or the use of ionic liquid, glycol and long time of reaction would prevent any development of these methodologies (especially the isolation of products) at a large scale.[2] Pentose-based surfactants are also gaining interest as efficient ingredients based on a waste valorisation philosophy.[3] In this context, carbohydrates represent a valuable feedstock in order to build surfactants but they need at first to be extracted from biomass and then purified before being chemically transformed with available methodologies. The extraction of carbohydrates from various sources of lignocellulosic biomass usually requires elevated temperatures and pressures.[4] This raises the energy demand of the overall surfactant process.[5] Applying lower temperature and atmospheric pressure limits equipments and energy costs, but imposes the use of high concentrations of acid (up to 100 wt% based on carbohydrate materials). This limits extraction yields and renders the overall cost of the process out of any market value.[6] The work presented in this paper browses some key data for a direct access to pentoses derived glycosides from biomass (Fig. 1). This methodology represents a real break through in the area of sugar based surfactants synthesis as it prevents all conventional biomass fractionation works that are inherent to prepare sugars in pure forms for chemists.

2. Experimental

2.1. Materials and instruments

Wheat bran was obtained from Chamtor (France). This material was used as received without any physical pretreatment. The composition of wheat bran as determined through NREL LAP,[7] was as follows: 22.4% glucan, 24.9% xylan, 13.2% arabinan, 1.3% galactan, 8.1% lignin, 5.90% ash, 15.44% protein, and 8.76% others by dry weight. All experiments were performed in duplicate under the same conditions and their average values were reported. n-decanol, H2SO4 (96%) and NaOH (50% solution) of analytical grades were used as received (Acros).

2.2. 2.2. Typical procedure for conversion of wheat bran hemicelluloses into alkyl-pentosides and quantification of glycosides

In a 1000 ml three necked round bottom flask, equipped with a magnetic stirring apparatus and a refluxing condenser, 100 g of wheat bran, 400 g of n-decanol, are progressively heated to the reaction temperature in a oil bath at atmospheric pressure. Sulfuric acid and distilled water are then added dropwise and the reaction medium is maintained under stirring (800 rpm). At the end of the reaction, the remaining solid is filtered off over cellulose filter. The residual sugar material is washed by acetone, dried at 90 °C under vacuum and weighed. Filtrate is neutralised by caustic soda solution to pH 9 (measured in a 10 wt% solution of water and isopropyl alcohol 1 : 1 v/v).

As the reaction products are rarely commercially available, alkyl glycosides standards were prepared by Fisher's glycosylation of D-xylose, and L-arabinose in n-decanol excess. Each of them was purified using column chromatography.[8] Their purities were checked by ^{13}C-NMR and1H NMR. The GC calibration was performed afterwards using these purified products (see

Agro-Industrie Recherches et Développement "Green Chemistry Department", F-51110, POMACLE, France. E-mail: b.estrine@a-r-d.fr
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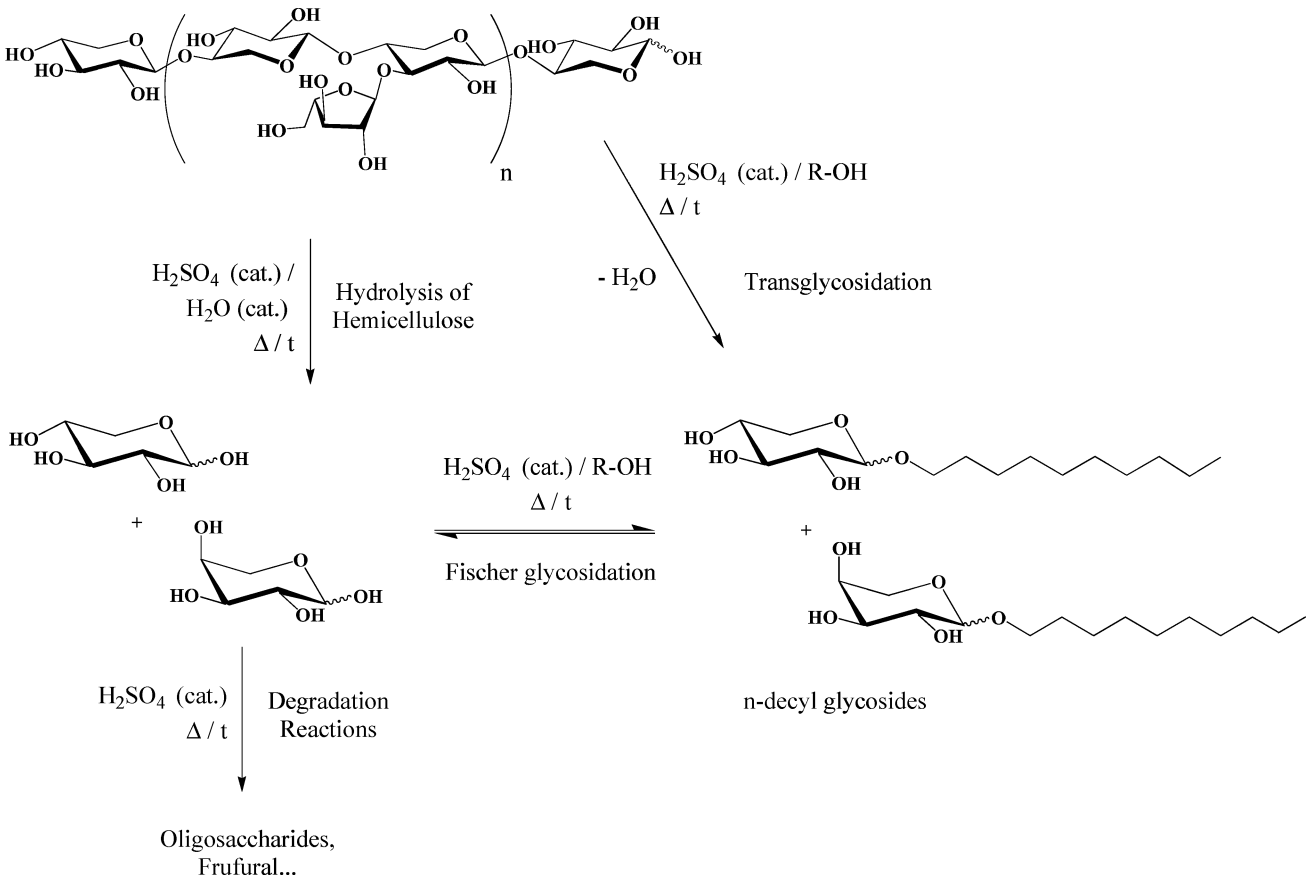

Fig. 1 Schematic illustration of the conversion of hemicelluloses into alkyl-pentosides (furanosides are omitted for clarity).

ESI for gas chromatography conditions and NMR spectra of standards and decyl-glycosides from wheat bran†).

2.3. Surface tension measurements

The critical micelle concentration (CMC) of the surfactants was determined with a KRUSS Processor tensiometer (K100) by the Wilhelmy method (KSV, Finland) using a platinum plate sensor in a jacketed cell. The temperature was controlled using a Julabo thermocontroller with an accuracy of 25 ± 0.5 °C. The surfactant solutions were stirred and allowed to stand for equilibrium at the set temperature before measuring the surface tension. The surface tension of the solutions was obtained as a mean value of ten measurements. The critical micelle concentration was graphically determined at the break of the curve of the surface tension measured *versus* the concentration of surfactants in solution.[9]

2.4. Foam properties

The foaming power is determined according to the Ross–Miles protocol derived from standard ISO 696 and AFNOR NFT 73–404, diluting the surfactant compositions (0.1% wt% in demineralised water) so as to represent the real conditions of foam creation during the use of a shampoo.[10] The method consists in measuring the volume of foam obtained after dropping, from a height of 450 mm, 500 mL of a solution of composition to be tested, onto a liquid surface of the same solution (100 mL). When the solution reaches the graduation mark (600 mL), the chronometer is then started. The volume of the foam is measured upon starting the chronometer and after 20 min. The volume of the foam is measured between the foam/liquid horizontal interface and the base of the foam/air interface.

2.5. Wetting power

The ability of a surfactant to wet textile substrates rapidly is a key performance property in many applications. The Draves Wetting test is a widely regarded laboratory procedure for ranking the relative wetting efficiencies of surfactants.[11] This test is a timed determination for the wetting of a cotton skein by dilute surfactant solutions, where short wetting times are indicative of excellent wetting efficiencies. A 0.1% active solution in deionized water of each surfactant was tested using standard cotton disc from Empa Materials.

3. Results

3.1. Synthesis of n-decyl glycosides from wheat bran

We carried out decyl-glycosides synthesis preparing dispersions of wheat bran (25 wt%) in n-decanol, at 100 °C and at atmospheric pressure during 1 h (Table 1, entries 1–5). The smooth conditions can be compared with high temperatures

Table 1 Synthesis of n-decyl glycosides starting from wheat bran at 90 °C

				n-decyl glycosides yields (%)[c]	
Entry	H_2SO_4[a]/H_2O[b]	Time/h	Temp./°C	Ara-C_{10}	Xyl-C_{10}
1	10/0	1	100	33.4	18.2
2	10/10	1	100	58.4	31.5
3	10/25	1	100	63.6	63.6
3	10/50	1	100	46.8	37.8
4	10/75	1	100	29.2	19.23
5	10/100	1	100	16.9	4.9
6	10/0	2	100	36.4	20.2
7	10/10	2	100	74.5	54.5
8	10/25	2	100	55	54
9	10/10	3	100	99.5	95.5
10	5/10	3	100	45.5	24.5
11	5/25	3	100	39	21
12	10/25	1	90	40.2	20.5
13	10/25	1	110	64.5	64.3

[a] Sulfuric acid wt% compared to wheat bran weight. [b] Water wt% compared to wheat bran weight. [c] Yield of monoglycosides determined by GC method.[8]

and pressures (165 °C, 20 bars) required for the synthesis of alkyl-glucosides from starch.[12]

At 10 wt% of sulfuric acid related to the sugar material, it is possible to reach a global glycosides yield of 63.6% when the water concentration is fixed at 25% (corresponding to 5.5 molar equivalent of water based on the available pentoses in the wheat bran; Table 1, entry 3). Below this water concentration, the yields of glycosides are lower, probably due to a low hydrolysis rate of the hemicelluloses. Although the arabinosides seem to be synthesized quickly (Table 1, entries 1, 2, 6, 7 and 9), this is probably due to the good availability of the arabinofuranose moieties along the xylooligosaccharide chains. When water concentration is higher than 25% (Table 1, entries 3–5), the glycosides yields measured are lower than 63.6%. Between 50 and 100% of water (corresponding to 11 and 38 equivalent based on pentoses), the glycoside yields constantly dropped to 16.9% for arabinosides, and 4.9% for xylosides. Here, the amount of water is probably lowering the rate of glycosylation, as the hydrolysis reactions (converting hemicelluloses or glycosides into monomeric sugars) are favoured in this conditions. At the end of the reactions, we detected low concentration of monomeric sugars (1% of xylose) and the n-decyl pentosides (arabinosides and xylosides) were observed as their α and β anomeric forms. Furfural was only detectable in the conditions of the entry 5 (concentration of 0.78% in the filtrate). We suggest here a one pot hydrolysis-glycosylation mechanism that is more probable in view of reports on the hydrolysis of xylan,[13] and glucosides manufactured from starch.[12] We have also carried out identical trials with an acid concentration of 20% (not reported in the table). We obtained glycosides yields similar to entry 3, Table 1, whatever the water concentration (from 0 to 100%). At this acid concentration, the hydrolysis step seems to be less limiting.

In order to optimize the conditions, we let the reactions proceed till 3 h. At 2 h, without addition of water, glycoside yields did not evolve significantly (compare entries 1 and 6, Table 1). When water concentration is 10% (2.2 molar equivalent based on pentoses), the glycoside yields are progressively improved. A quasi-complete conversion of sugars into their corresponding alkyl-glycosides is reached at 3 h (entries 7 and 9, Table 1). At 25% of water, we observed a diminution of the glycosides yields during the second hour of reaction, probably caused by hydrolysis. We also tried to below the acid concentration till 5% (entries 10 and 11, Table 1), or looked at lower and higher temperature (entries 12 and 13, Table 1), but no more improvement was noticeable.

The high purity of decyl glycosides was confirmed after separation over flash chromatography on silica gel of the filtrate obtained in trial 9 of Table 1 (following the method used for GC internal standard preparation). Pollutants such as sulfated ashes and proteins were analysed on the crude mixture of trial 9 obtained after excess of alcohol was distilled off (respectively 4 wt%, and 5.6 wt%; protein content obtained following the Kjeldhal method). The crude glycosides thus obtained contain also 0.6% of xylose and 1.6% of remaining decanol. The wheat bran residue recovered from the experiment of entry 9, Table 1, was analysed following the same techniques used to determinate the composition of the starting raw material. The results were as follows: 36.8% glucan, 1.3% xylan, 0.9% arabinan, 0.3% galactan, 9% lignin, 10.90% ash, 16.6% protein, and 24.2% others by dry weight. Here, we confirm the good conversion of hemicelluloses. It is also important to notice that the protein and lignin concentrations are equivalent to the starting wheat bran, whereas the cellulose concentration raised to 36.8% (22.4% in the starting wheat bran). The remaining material is potentially a good raw material as a potential low cost source of glucose for other valorisation such as the production of bioethanol or added value chemicals such as hydroxymethyl furfural (HMF).

3.2. Surface active properties of the glycosides mixture obtained from wheat bran at an air/water interface

The favourable performance properties of surfactants, in particular interfacial properties and behaviour in solutions (for example, phase behaviour), are essentially attributable to specific physicochemical effects.[14] The surface tension of alkyl glycosides from wheat bran was investigated and compared to alkyl glycosides obtained by Fisher's glycosylation (Table 2). Concerning the critical micelle concentration (CMC) of glycosides surfactants, that is a good cursor of the surfactant efficiency, it is clear that xylosides containing compositions (from wheat or from pure D-xylose) show the best results. This behaviour is explained by the fact that xylosides are more hydrophobic substances when compared to glucosides and so tend to aggregate at lower concentrations.[15] Obviously, due to the presence of impurities in the glycosides directly obtained from biomass, their CMC is higher than pure D-xylosides and so are less efficient. Inorganic pollutants and proteins are present in the wheat bran-based surfactants. This lowers the concentration of surface active glycosides in the crude composition. In brief, although the wheat-based surfactants are less efficient, they remain more suitable than glucose-based chemicals for application in detergents. All glycosides compositions studied showed similar effectiveness (displayed by surface tensions at CMC comprised between 26 and 28 mN m^{-1}). The decyl glycosides from wheat bran showed similar production

Table 2 Surface properties, foaming and wetting power of glycosides composition from wheat bran

Surfactant	CMC/mg L^{-1}	γCMC/mN m^{-1}	Foam volume at $t = 0$/mL [Stability at 20 min (%)]	Wetting time/s
n-Decyl-glycosides from wheat bran (table 1, entry 9)	493	27.7	470 [61]	36
n-Decyl xylosides from D-xylose	301	28	480 [75]	23
n-Octyl/n-decyl polyglucosides[16]	963	26	450 [75]	196

of foam (foam power) compared to pure D-xylosides. The main consequence of the presence of impurities is displayed by the foam stability that dropped from 75% for the D-xylosides to 61% for the crude surfactants from wheat bran. This lower foam stability could be a bottleneck for cosmetic application, but it can be a serious advantage for detergent manufacture, especially when detergent products are to be non-foaming to keep the rinsing process efficient and where high foaming surfactants are less considered as potential ingredients. Another noticeable consequence of impurities is that the wetting time is raised from 23 s for pure D-xylosides to 36 s for wheat glycosides. However, this latter value remains at an acceptable level if compared with a commercial alkyl oligoglucoside. Obviously, although the surface activity and foam properties of wheat-based surfactants are interesting, in view of an industrial use, it would be next necessary to check whether impurities of these crude mixtures are compatible with the other targeted formulation ingredients and in particular in the field of detergents.

4. Conclusion

In conclusion, we have shown that the conversion of wheat bran hemicelluloses into alkyl monoglycosides with high yields is possible *via* a single step operation. We carried out this reaction under smooth conditions. The yields of n-decyl xylosides and arabinosides thus obtained are a clear improvement compared to previous results on conversion of starch into alkyl glucosides,[12] and are also much higher than those reported by enzymatic processes for the conversion of xylan into alkyl xylosides.[17] The remaining material is preserved keeping all its promises as potential feedstock for fuels or value added platform chemicals like HMF. The wheat-based surfactants thus obtained without further purification have shown good surface properties considering its purity. In view of the growing importance of molecules based on renewable resources in the detergents and cosmetics industries, this approach may open a new avenue for the production of green surfactants.

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