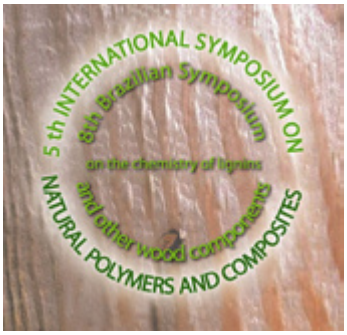

Beechwood Hemicelluloses-based Polymeric Surfactants

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Abstract: *New water-soluble amphiphilic glucuronoxylan derivatives were synthesised by unconventional methods based on the reaction with (A) vinyllaurate and with (B) mixed anhydride, prepared 'in situ' from acetanhydride and lauric acid, using two glucuronoxylan (GX) preparations. The derivatives were characterised by spectral methods (FT-IR and NMR) and their surface-activity was tested for surface tension, and emulsifying and foaming effects. The water-solubility and efficiency of the new functional properties were shown to depend not only on the degree of substitution by lauroyl substituents but also on the supermolecular structure of the starting GX samples having different proportions of glucuronic acid side chains. The derivatives represent biosurfactants with potential use in food products, cosmetics, pharmaceuticals and other technical applications.*

Keywords: *Hemicellulose; Glucuronoxylan; Esterification;Polymeric Surfactant.*

The growing demand for natural and biodegradable surfactants had evoked a renewed interest in amphiphilic polysaccharide derivatives based on various commercial and non-commercial polysaccharides. Among the last group hemicelluloses, the most abundant cell wall polysaccharides next to cellulose, represent a hitherto unexploited biopolymer. In the lignified tissues of dicotyl plants [1] 4-O-methylglucuronoxylan is the main hemicellulose representative. The water-soluble GX isolated from beechwood meal has been reported [2] to exhibit tensioactive properties in dependence on the proportion of closely associated and/or bound lignin acting as hydrophobic sites. In order to prepare amphiphilic xylan-based derivatives, partial hydrophobisation of various xylans was performed by etherification reactions using long chain alkyl halides or *p*-carboxybenzyl bromide [3,4] and, recently, by conventional esterification using stearoyl chloride [5].

In continuation of our research on functionalisation of xylan-type polysaccharides, we report on the hydrophobisation of beechwood glucuronoxylans using non-conventional esterification reactions.

Materials and methods

As starting materials, the water-insoluble glucuronoxylan (GXL, Xyl:GlcA=40:1) a by-product of viscose production form beech sulfite pulp (Lenzing AG, Austria), and the water-soluble glucuronoxylan (BGX, Xyl:GlcA=12:1) from beechwood meal (Institute of Chemistry, SAS, Slovakia) were used.

The unconventional esterification methods were based on the reaction of the xylans in the DMF/pyridine medium with and without dimethylaminopyridine as catalyst using (A) transesterification with vinyllaurate [6] and (B) esterification with mixed anhydride, prepared 'in situ' from acetanhydride and lauric acid [7]. The derivatives were characterised by FT-IR spectra in KBr (NICOLET Magna 750 spectrometer, resolution of 4 cm^{-1}) and ^{1}H- and ^{13}C-NMR spectra in D_2O or DMSO-d_6 (Bruker DPX AVANCE-300 spectrometer operating at 300 MHz for ^{1}H and 75.46 MHz for ^{13}C). The surface-activity testing methods were described in [3]. The spectral data were used to estimate the degree of esterification (DE).

Results and conclusions

Esterification of the GXL and BGX by methods (A) and (B) yielded lauroyl and mixed acetyl/lauroyl esters, respectively. The reaction conditions were directed to achieve rather low DEs and prepare water-soluble products. The introduction of the long-chain ester groups into the xylan chains affected differently their water-solubility, an essential attribute for their applicability as polymeric surfactants. GXL was water-soluble at low DE (0.2-0.4) and became insoluble at higher DE. The same effect was observed after esterification of GXL with stearoyl chloride [5]. It can be explained by changes of the supermolecular structure due to the existence of randomly distributed acyl groups. These prohibit the aggregation tendency of unbranched xylan chains through intermolecular hydrogen-bond formation during the isolation and drying processes. It was documented by the FT-IR spectral pattern changes in the region of stretching OH vibrations and supported also by the thermal stability/DS dependence of GXL esters [5]. In contrast to GXL, BGX esters became water-insoluble at higher DE (~ 0.6) because of the substantially higher content of the anionic glucuronic acid substituents, affecting the hydrophilic/hydrophobic balance.

The surface tension values of the water-soluble derivatives, prepared from both GXL and BGX, in dependence on the

DE showed only a moderate decrease to ~ 55 mN m^{-1}. However, the aqueous solutions of some of the derivatives gave emulsions of the oil/water type with excellent emulsifying efficiency comparable to that of the commercial emulgator Tween 20. Similarly as in the case of C_n-alkyl ether derivatives prepared from BGX [3], the BGX lauroyl esters showed remarkable foaming activity, whereas the GXL esters gave unstable foams.

When comparing both non-conventional methods, the transesterification with vinyllaurate was the more effective one. Esterification with the mixed anhydride gave derivatives with acetyl groups prevailing over the lauroyl substituents, resulting in lower surface activity.

The results suggested that under suitable reaction conditions, water-soluble derivatives with acceptable surface-active properties can be prepared from both xylan preparations and might be useful as biosurfactants in various practical applications. Due to the relatively low amount of the introduced ester functions, the biodegradability of the derivatives should not be changed.

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