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Chemical modification of corn fiber with ion-exchanging groups ☆

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ABSTRACT

Corn fiber was chemically modified with ion-exchanging groups to prepare water-soluble polysaccharides. The soluble fractions were dialyzed using dialysis tubing (1 kDa) and the material retained inside the tubing was filtered through 10 kDa membranes to separate into fractions with molar mass of 1–10 kDa and greater than 10 kDa. The yield of solubilized material of molar mass higher than 10 kDa (47%) and 1–10 kDa (17%) obtained by sulfonation in the presence of NaOH under vacuum was greater than the yields of the treatment at the ambient pressure (43% and 2%) and also in experiments run with only KOH (40% and 5%) or NaOH (38% and 5%) at ambient pressure. The sugar analysis indicated that they were typical glucuronogalactoarabinoxylans containing 46–57% D-xylose (Xyl), 25–33% L-arabinose (Ara) and 6–12% D-galactose (Gal).

1. Introduction

Corn fiber (CF) and corn bran (CB) are the main low value by-products of the corn wet- and dry-milling processes, respectively. Corn fiber is an agro-based fiber and primarily composed of cell-wall non-starch polysaccharides derived from corn kernel pericarp and/or endosperm tissues. The corn fiber is the main source of corn fiber gum (CFG) which is an arabinoxylan and its suggested uses are as adhesive, thickener and stabilizer (Wolf, MacMasters, Cannon, Rosewell, & Rist, 1953) and a film former and emulsifier (Whistler, 1993). The detail emulsifying properties and the structure function relationship of CFG is well studied and reported by Yadav, Fishman, Chau, Johnston, and Hicks (2007a), Yadav, Johnston, and Hicks (2007b), Yadav, Johnston, Hotchkiss, and Hicks (2007c), Yadav, Moreau, and Hicks (2007d). Research on polysaccharides modification is focused on new functional polymers for applications in various fields. In comparison to cellulose, the literature on chemical modification of hemicelluloses is less developed (Schwikal, Heinze, Ebringerova, & Petzold, 2006; Šimkovic, Mlynár, & Alföldi, 1990; Šimkovic, Mlynár, & Alföldi, 1992) despite the fact that hemicellulose is quite abundant, making up to one third of the dry weight of annual plants/agricultural crops (Whistler, 1953).

In the present study CF was treated with alkali and simultaneously modified with cationic or anionic ion-exchanging groups with the goal to prepare chemically modified water-soluble material for making biodegradable films, superior emulsifiers, and other food and industrial materials. They could replace gum arabic due to lower price and better properties. To learn more about utilization in particular first the properties of individual materials must be compared. That is why we have used modification procedure based upon an evaporation of the reaction mixture under vacuum to accelerate reaction rate. This is because water causes hydrolysis of the alkylating agent which lowers the yield of the modified product. For confirmation also parallel experiments at ambient pressure were run. By the chemical modification with glycidyltrimethylammonium chloride (GTMAC) or 3-chloro-2-hydroxypropanesulfonic acid, sodium salt (CHPS) two structurally similar ion-exchanging groups were introduced differing in charge type. This resulted in solubilization of part of CF. The soluble fraction was dialyzed through 1 kDa MWCO dialysis tubing and membrane filtered through 10 kDa to prepare polysaccharide fractions of molar mass 1–10 kDa and over 10 kDa. Samples were analyzed by NMR and elemental analysis to prove the chemical linkage of ion-exchanging groups to carbohydrates.

2. Materials and methods

2.1. Materials

The oven dried corn fiber sample was kindly provided by ADM Research. They were extracted with hexane to remove oil (Moreau, Powell, & Hicks, 1996) after grinding to a 20-mesh particle size using a Wiley mill. Starch was removed from the 20-mesh de-oiled fiber by treating with Termamyl α-amylase (Doner, Chau, Fishman,

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& Hicks, 1998). Glycidyltrimethylammonium chloride (GTMAC, Fluka), 3-chloro-2-hydroxypropanesulfonic acid, sodium salt (CHPS, Aldrich) and all other chemicals were used without further purification.

2.2. Chemical modification of corn fiber

Alkylating agents (GTMAC or CHPS, 0.5 g) and alkali (NaOH or KOH, 0.5 g) were mixed with de-oiled and de-starched corn fiber (0.5 g) and water (5 mL) in a round bottom flask. The mixture was run on a rotary evaporator at 60 °C under vacuum (3.3–4 kPa) or at ambient pressure for 3 h. The reaction mixture was filtered by using a fritted glass funnel (G4, Koch-Light) and separated into a soluble fraction and residue. The soluble fraction was neutralized with HCl and dialyzed using a 1 kDa MWCO dialysis tubing (Spectra/Por®) to get rid of all impurities and unreacted reagents but to retain any product bigger than 1 kDa. The reaction mixture retained in the dialysis tubing was filtered through a membrane filtration system (10 kDa, Amicon under nitrogen pressure of 3.5 kg/cm^2) to separate the products of molar mass 1–10 kDa and greater than 10 kDa. The two soluble fractions and residue were separately collected, evaporated, freeze dried and weighed.

2.3. Analysis

The monosaccharide analysis was performed by high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) using methanolysis combined with trifluoroacetic acid (TFA) hydrolysis (Yadav et al., 2007b). The elemental analysis was done on a Fisons EA-1108 instrument. NMR measurements were performed in D_2O at 25 °C on Varian 600 MHz UNITY INOVA spectrometer equipped with 5 mm 1H {13C, 15N} PFG Triple Res IDTG600-5 probe head. ^{1}H and ^{13}C chemical shifts are referred to 3-(trimethylsilyl)-propionic acid (TSP) internal standard. Multiplicity edited ^{1}H–^{13}C HSQC spectra were recorded in phase-sensitive pure absorption mode with optimization on one bond coupling constant $^1J_{CH} = 165$ Hz. ^{1}H–^{1}H COSY spectra with gradient selection and ^{1}H–^{13}C HMBC spectra were measured in absolute intensity mode. The spectral widths employed in 2D NMR experiments were typically 6000 Hz (^{1}H) and 20000 Hz (^{13}C), respectively.

3. Results and discussion

3.1. Fractionation and chemical modification of corn fiber

All the experiments run are presented in two schemes differing in used base. The yields of soluble fractions obtained with NaOH extraction at ambient pressure were higher than under vacuum (Fig. 1). But the yields of 1–10 kDa fractions (shown in brackets) as well as the residues (R_1 and R_2) obtained from NaOH extractions under vacuum and at ambient pressure were similar. The introduction of the anionic group, 2-hydroxypropylsulfonate (HPS) to CF under vacuum gave higher yields of both higher (> 10 kDa) and lower (1–10 kDa) molar mass soluble fractions which could be due to an alkaline degradation during concentration of the reaction mixture. The sulfur content was slightly higher in the fractions obtained under vacuum than at ambient pressure extraction (VE_2 1.91%, E_2 0.60%, VR_2 0.80% and R_2 0.45%). The introduction of a cationic group on CF by quaternization with GTMAC produced less of soluble fractions than introduction of an anionic HPS group under identical conditions of base concentration, vacuum and temperature. The treatment of CF with NaOH in the presence of GTMAC produced more of soluble fractions (26% of above 10 kDa and 10% of 1–10 kDa material) at the ambient pressure than under vacuum (9% and 2%). The nitrogen content of fractions obtained under vacuum (1.51% and 2.40%) was higher than the fractions obtained at ambient pressure (1.43% and 1.86%). The yield of the residue was higher when the extraction was done in presence of GTMAC or with mixture of GTMAC and CHPS under vacuum than at ambient pressure. On the other hand the results were very close to each other at both conditions when the extraction was carried out in absence of any alkylating agent or in presence of CHPS. When the extraction was done in presence of both alkylating agents, the yield of soluble high molar mass fraction (32%) obtained at ambient pressure was bigger than under vacuum (14%), but it was not as high as obtained in presence of CHPS (43% and 47%, respectively). A slightly more of lower molar mass (1–10 kDa) material was found in the extraction done under vacuum than at ambient pressure which can again be due to alkaline degradation during reaction mixture concentration. Based on the presence of nitrogen and sulfur in the modified product, the degree of quaternization and sulfonation carried under vacuum (1.30% of nitrogen and 1.08% sulfur in VE_4) was similar to one done at ambient pressure (1.22% and 0.98% in E_4).

When extraction of CF was run in analogical way, but with KOH (Fig. 2), more of the material was extracted at ambient pressure than under vacuum. It was more than the yield obtained with NaOH extraction run under similar conditions. The yield of high molar mass soluble fraction under vacuum extraction with KOH was lower than extraction with NaOH. The amount of both soluble fractions extracted with KOH in presence of CHPS were almost the same under both vacuum (33% and 16%) and ambient pressure (32% and 16%) conditions although less of total materials were solubilized than by NaOH treatment. Quaternization of CF at ambient pressure gives more soluble materials in presence of KOH than NaOH. Dramatic decrease in the large molar mass fraction (1%) is seen in extraction with KOH in presence of GTMAC under vacuum, which could be due to degradation of higher molar mass products with concentrated alkali. Alkaline degradation is confirmed by the

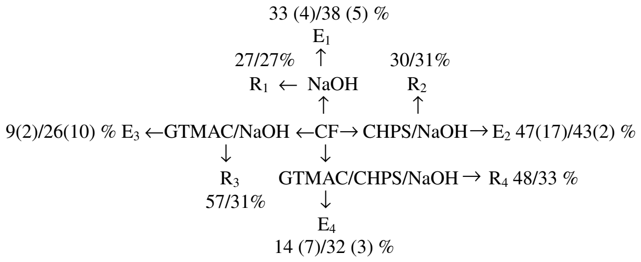

Fig. 1. Percent yields of CF fractions extracted with NaOH with and without alkylating agents under vacuum/ambient pressure. Yields of fractions of molar mass >10 kDa are given out side the brackets and 1–10 kDa inside the brackets. Weight percent is based on de-oiled and de-starched corn fiber. Extracts and residues are indicated by E (E_1, E_2, E_3 and E_4) and R (R_1, R_2, R_3 and R_4), respectively.

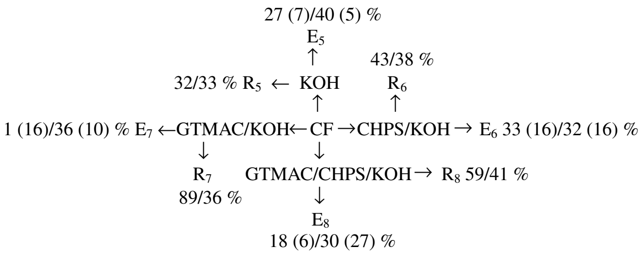

Fig. 2. Percent yields of CF fractions extracted with KOH with and without alkylating agents under vacuum/ambient pressure. Yields of fractions of molar mass >10 kDa are given out side the brackets and 1–10 kDa inside the brackets. Weight percent is based on de-oiled and de-starched corn fiber. Extracts and residues are indicated by E (E_5, E_6, E_7 and E_8) and R (R_5, R_6, R_7 and R_8), respectively.

increased yield of low molar mass fraction. The amount obtained by modification with a mixture of both alkylating agents at ambient pressure was slightly smaller than by sulfonation. Over all, the sulfonation in the presence of NaOH and at ambient pressure gave the highest yield of soluble fractions. The incorporation of ion-exchanging groups were similar for experiments run in presence of NaOH or KOH. The 1–10 kDa-fractions had higher content of nitrogen and sulfur than fractions over 10 kDa.

3.2. Monosaccharide composition

The general sugar composition of NaOH and KOH extracts under vacuum and at ambient pressure do not differ significantly from the original CF sample (Table 1). They all show a typical arabinoxylan structure with an Ara/Xyl ratio ranging from 0.5 to 0.7, which is typical for arabinoxylan from corn fiber (Yadav et al., 2007b). A slightly low Ara/Xyl ratio (0.44) in extract E_8 may be due to loss of some of Ara during alkaline extraction/chemical modification treatment. They contain about 25–33% Ara, 46–57% Xyl, 6–9% Gal, 0–6% Glc, 0–8% GlcA and trace amount of Fuc, Rha and GalA in some samples which are very similar to the sugar composition reported for the alkaline extract of CF by Yadav et al. (2007b). The detection of some Glc in these samples may be an indication of some residual alkali soluble starch, cellulose, glucan or xyloglucan. The residues (R_6 and R_7) left after alkaline extraction of CF has a high Glc content (24–28%) in addition to 17–21% of Ara and 34–42% of Xyl with Ara/Xyl ratio of 0.50. These residues are very much similar in carbohydrate composition to cellulose/arabinoxylan (Doner & Johnston, 2001) which is suggested for a potential food application as a bulking agent.

3.3. NMR study

In Fig. 3 there are NMR spectra of low molar mass (1–10 kDa) soluble fraction (E_1, Fig. 1) obtained from dialyzing NaOH extract using 1 kDa MWCF dialysis tubing. There are four signals in the anomeric region of HSQC spectrum (Fig. 3A) at 107.20/5.11, 108.50/5.25, 108.10/5.30 and 107.50/5.42 ppm which might be related to arabinose units similarly like observed on wheat endosperm (Hoffmann, Kamerling, & Vliegenhart, 1992). The signal at 101.30/4.51 ppm seems to belong to C/H-1 of Xyl units and signal at 99.20/5.03 ppm could be attributed to C/H-1 of GlcA unit (Šimkovic, Alföldi, & Matulová, 1986). The signals at 61.30/3.80, 62.90/4.15 and 62.60/3.39 as well as 65.20/4.00 and 65.20/3.36 ppm belong according to multiplicity edited HSQC (in red for PDF file) to CH_2 groups of Xyl and Ara units. According to COSY (data not shown) the C/H-2 signal of the xylan main chain is at 72.80/3.31 ppm and the three C/H-2 signals of differently branched Ara units are at 81.00/4.20, 84.40/4.17 and 84.80/4.32 ppm. Additionally the COSY spectrum indicates that Xyl unit H3 is at 3.56 ppm, which correlates with peak at 73.60 ppm in Fig. 3A. The most intense CH_2 group signal at 61.30/3.80 ppm correlates with signal 81.00/4.20 ppm through HMBC signals at 3.97 ppm (Fig. 3B). Due to the intensity we assume that it is the signal of Xyl unit with correlation from C5 to H3 as well as C2–H3. There is also an evident correlation of anomeric Ara signal with C2 peaks at 84.40 and 84.80 ppm.

Retentate from membrane filtration of the hydroxypropylsulfonated sample (Table 1, E_2) analyzed with NMR gave a HSQC spectrum (Fig. 4A) which contained CH_2 group signals according to multiplicity edited HSQC at 54.70/3.11, 62.10/3.77, 65.35/3.69, 65.70/3.59, 65.70/4.00 and 65.70/3.33 ppm. The new signals in comparison to unmodified sample E_1 are CH_2 groups at 54.70/3.11, 65.35/3.59 and 65.70/3.69 ppm. Additional new signals are at 67.35/4.28 and 70.00/3.66 ppm, which we ascribe to CHOH groups. According to HMBC (Fig. 4B) the substituent signals are in correlation with signal at 71.80/4.16 ppm. According to COSY this peak belongs to Ara C/H-2 units. The CH_2 signals at 65.35/3.69 and 3.59 ppm are also in correlation with C/H-5 of Ara at 65.70/4.00 and 3.33 ppm. There is also a less intense correlation between a signal at 74.80/4.19 ppm and the substituent. According to COSY the signal belongs to C/H-2 of Xyl unit. These results confirm the predominant linkage of the substituent to C2 of Ara unit and the less abundant linkage to some Xyl units.

The small molar mass fraction (1–10 kDa) obtained from GTMAC/NaOH quaternization of CF (Fig. 1; E_3) gave a HSQC spectrum with three new CH_2 group signals (Fig. 5A) according to multiplicity edited HSQC (at 72.90/3.63; 71.70/3.68 and 68.30/3.51 ppm) of the $\text{-}CH_2CHOHCH_2N^+(CH_3)_3$ substituent. The additional new signals are at 65.25/4.44, 69.70/3.67 (CHOH) and 54.30/3.25 (CH_3) ppm. According to COSY (data not shown) there is a C/H-2 signal at 73.00/3.37 ppm which we ascribe to Xyl unit. This signal is in correlation with HMBC signal at 3.57 ppm (Fig. 5B), which is in correlation with CH_2 group of the substituent at 72.90/3.63 ppm (Fig. 5A). This indicates a substitution of the quaternary group on C2 of Xyl. The Ara C/H-5 signals at 63.30/4.12 and 3.42 as well as 65.25/4.02 and 3.37 ppm are similar to signals detected in the unmodified sample. The last two of them are in correlation with the signal at 3.50 ppm of the HMBC spectrum (Fig. 5B). This signal is also in correlation with CHOH group of the substituent in the HSQC spectrum at 65.25/4.44 ppm as well as with the methyl group at 54.30/3.25 ppm. The intensity of the C/H-2 correlated peaks of Xyl units is stronger than of C/H-5 signals of Ara linked to the substituent, which is in correlation with monosaccharide composition analysis. Additionally there are two C/H-2 signals (77.30/3.93 and 80.90/4.17 ppm) which we ascribe to Ara unit and were present also in the unmodified fractions. They are not in correlation with the substituents and we assume they are not substituted.

Table 1
Monosaccharide composition of samples (mol.%).

Samples[a]	Ara	Gal	GalA	Rha	GlcA	Xyl	Fuc	Glc
CF[b]	30	7	1	0	3	54	0	5
VE_1[c]	30	7	0	1	5	55	0	2
E_1	33	6	1	2	6	51	0	1
VE_2	29	6	0	1	5	55	0	3
E_2	30	7	1	1	6	52	1	3
VE_3	29	6	1	1	6	54	1	2
E_3	32	6	1	1	7	51	0	1
VE_4	27	7	1	1	6	54	1	2
E_4	28	6	1	1	6	56	0	2
VE_5	31	7	0	1	5	54	1	2
E_5	31	7	1	1	6	53	1	1
VE_6	29	7	0	1	5	56	0	1
E_6	29	8	1	1	6	53	1	2
VE_7	30	7	0	0	3	54	0	6
E_7	28	6	4	1	6	53	0	2
VE_8	32	9	1	2	8	46	1	2
E_8	25	6	1	1	6	57	0	3
R_7	17	12	0	2	3	34	5	28
R_6	21	9	3	0	3	42	0	24

[a] The samples abbreviations are as in Figs. 1 and 2.

[b] Corn fiber used for modification.

[c] Abbreviation with E and VE indicate the extraction at ambient pressure and under vacuum, respectively.

4. Conclusions

The yield of alkaline extract of pretreated (de-starched and defatted) CF can be increased up to 47% by one step chemical modification/extraction with alkali in the presence of an ion-exchanging alkylating agent. The alkali extracted soluble fractions are typical

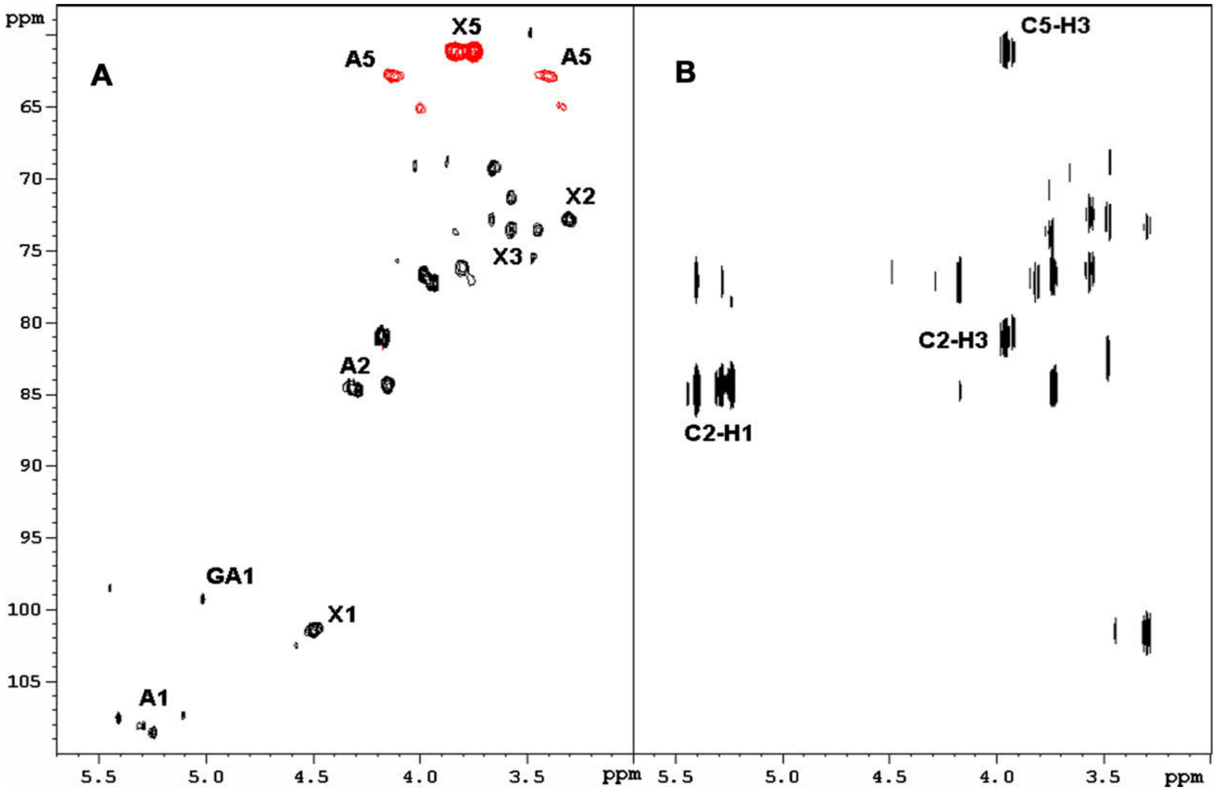

Fig. 3. HSQC (A)/HMBC (B) spectra of the low molar mass (1–10 kDa) NaOH extract E_1. The symbols A1, A2, A5, X1, X2, X3 and GA1 are related to arabinose, xylose and glucuronic acid individual signals as ascribed in the text.

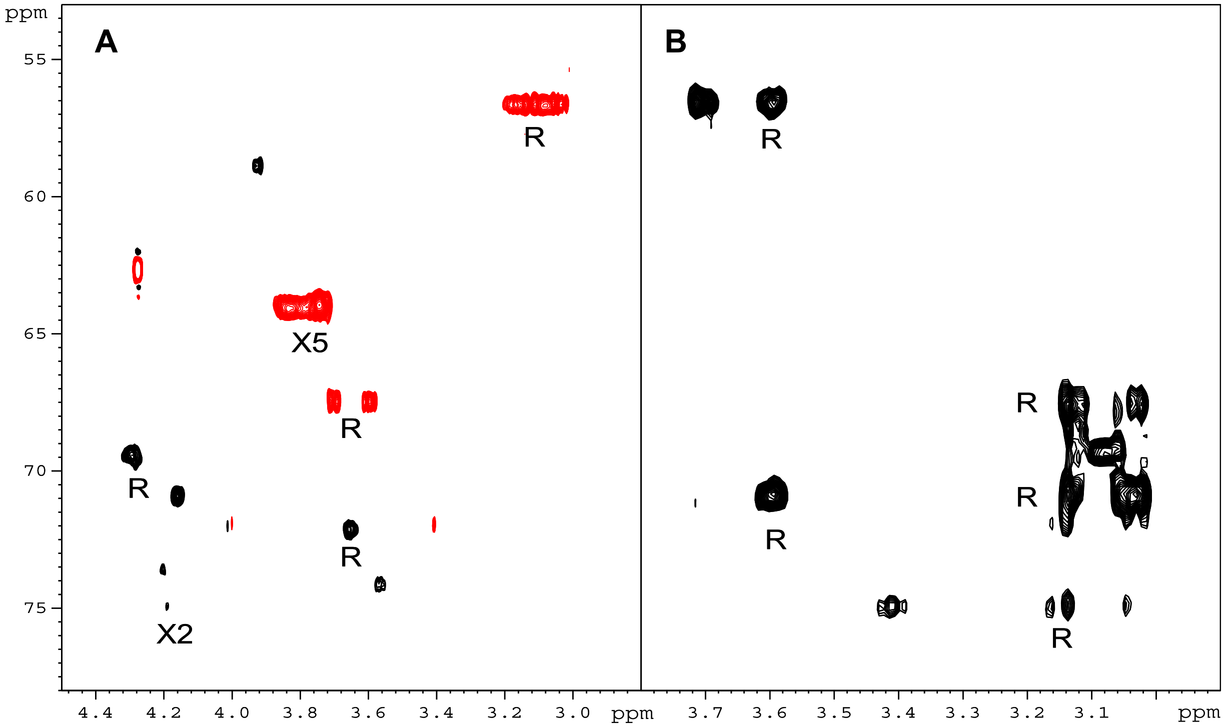

Fig. 4. HSQC (A)/HMBC (B) spectra of hydroxypropylsulfonated fraction (Table 1, E_8. The symbols are the same as in Fig. 3; R stands for signals related to the substituent.

glucuronogalactoarabinoxylans with Ara/Xyl ratio of about 0.5–0.7. The residue obtained from alkaline extraction consists of cellulose and arabinoxylan. The linkage of the substituents was confirmed by elemental analysis and NMR spectroscopy. The low molar mass (1–10 kDa) alkaline extract obtained from sulfonation of CF represents about 1/3–1/2 of the total yield.

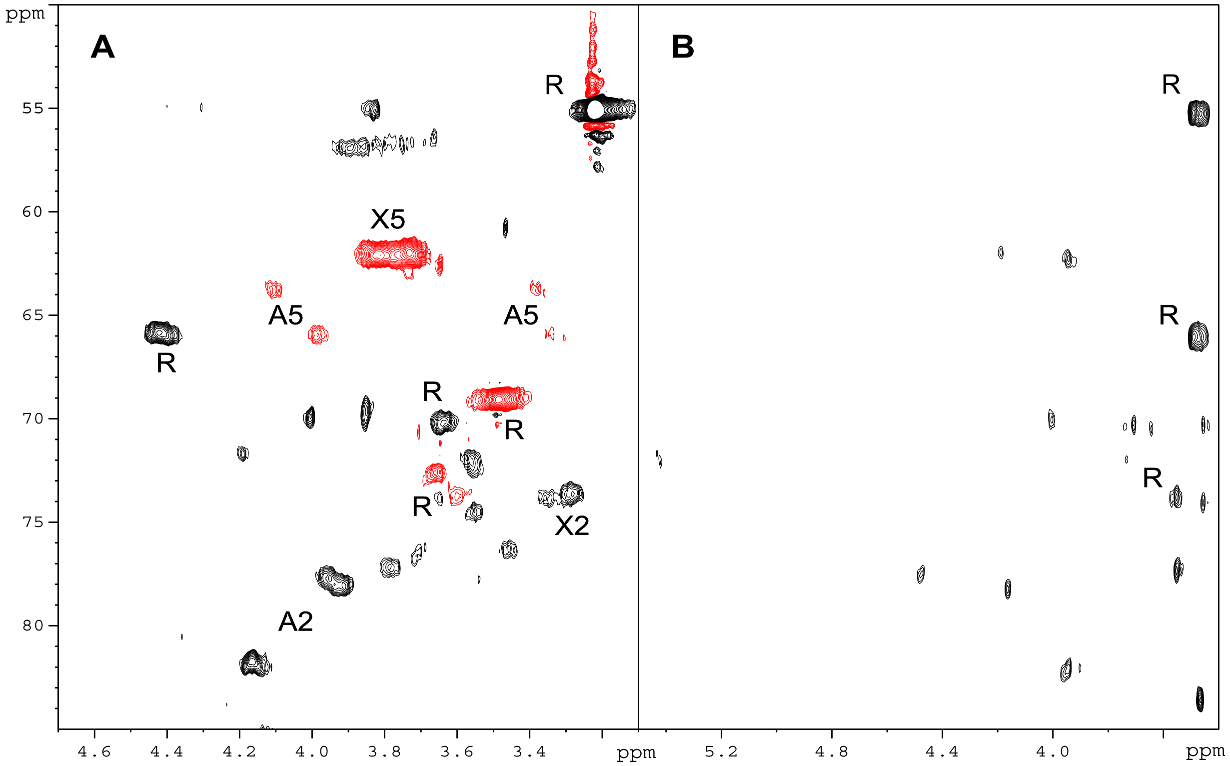

Fig. 5. HSQC (A)/HMBC (B) spectra of the low M_w (1–10 kDa) fraction E_2 quaternized with GTMAC/NaOH. The symbols are the same as in Fig. 3; R stands for signals related to the substituent.

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