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Preparation and characterisation of methylated hemicelluloses from wheat straw

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Abstract

Wheat straw hemicellulose ether was prepared by methylation with methyl iodide using sodium hydride as a catalyst reacted in dimethyl sulphoxide. The degree of substitution (DS) was determined by elemental analysis. According to the elemental analysis data, the DS-value can be calculated; it was 1.7. The structure of the methylated hemicellulose formed was characterised by nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopy. The thermal properties of the prepared ether were studied by simultaneous thermal analyser (STA 625). Differential scanning calorimetry (DSC) was also used to determine the thermal profile of the material degradation. It was found that the thermal stability of wheat straw hemicellulose ether increased by methylation.

Keywords: Xylose; Methylation; Hemicelluloses

1. Introduction

Over 3000 million tonnes of cereal straw is produced in the world per annum. The agricultural crop residues represent an enormous under-utilised resource, especially wheat straw, of which approximately 170 million tones are produced yearly in Europe. These amounts are significant enough to consider wheat straw as a generic source of renewable materials, particularly for the production of chemical derivatives from cellulose, hemicelluloses and lignin (Montane, Farriol, Salvado, Jollez & Chornet, 1998).

Wheat straw contains 14–15% lignin, 35–40% cellulose, and 30–35% hemicelluloses. The hemicelluloses are made up of a (1 → 4) linked β-D-xylan main chain with L-arabinofuranosyl and D-xylopyranosyl side chains attached at position O–C(3), and D-glucopyranosyluronic acid (or 4-*O*-methyl-D-glucopyranosyluronic acid) groups attached at position O–C(2) (Sun, Lawther & Banks, 1996; Wilkie, 1979). The backbone contains β-D-xylopyranose units, each of which has two hydroxyl groups available for modification. The hydroxyl groups allow the potential for esterification, etherification, oxidation and other reactions such as hydrolysis and reduction. Some hemicellulose derivatives have been prepared by using these reactions and various reagents. For example, Croon and Timell (1960a,b) reported the methylation of a 4-*O*-methyl glucuronoxylan with dimethyl sulphate, finding that HO–C(2) was more reactive than HO–C(3). A series of carboxymethyl ethers with DS varying from 0.13 to 0.92 was prepared by Schmorak and Adams (1957) from beechwood xylan. Sjöström (1989) showed in the carboxymethylation of hardwood pulps that xylan was carboxymethylated to a higher DS than cellulose. Also, the HO–C(2) was much more reactive than the HO–C(3) by a factor of 2.4 and 3.3 for the xylan and cellulose components, respectively (Lai, 1996). Manzi and Cerezo (1986) concluded from the methylation of galactomannans in organic media, that the extent of reaction was significantly influenced by the orderly structures of the polymer. The chemical and physical properties of the derivatives are influenced by the types of substituent, the degree of substitution (DS), the uniformity of substitution, the degree of polymerisation (DP) and the distribution of molecular weight (Ishizu, 1991).

The DS is defined as the average number of hydroxyl groups substituted in an anhydroxylose unit, the maximum DS is 2. The nature of substituents influences both the physical and chemical properties. Physical properties such as solubility and swelling are strongly affected by changing the DS. The uniformity of substitution depends upon equal derivatisation along the hemicellulose chain. This is mediated by the relative reactivities of hydroxyl groups, which depend on a steric factor and by the homogeneity

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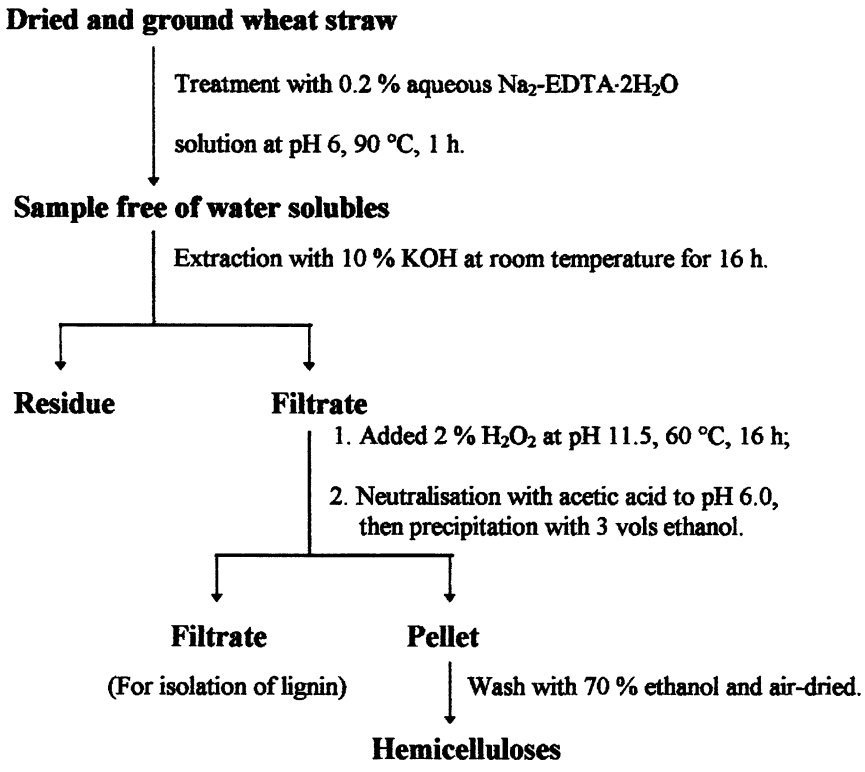


Fig. 1. Scheme for extraction of wheat straw hemicelluloses by H_2O_2.

of the reaction. Since the derivatisation of hemicelluloses is generally conducted under homogeneous conditions, all hydroxyl groups along a hemicellulose chain are equally accessible to reagents. In order to realise this aim, the following method has been proposed especially for etherification and for methylation: (1) use of the strongly basic methylsulfinyl carbanion in a non-aqueous medium to generate the polysaccharide alkoxide; (2) use of hemicelluloses, which are soluble in an organic solvent, such as dimethyl sulphoxide (DMSO), as a starting material for etherification performed under alkaline conditions; (3) use of non-aqueous hemicellulose solvents as a reaction medium. Wheat straw hemicelluloses were methylated by the above procedure. The product was examined using various analytical techniques.

2. Experimental

2.1. Materials

Wheat straw was obtained from Compak Co. (Gainsborough, England). The straw was first ground in a Christie laboratory mill to pass a 0.7 mm size screen, then stored at 5°C until use. Sodium hydride (NaH), dimethyl sulphoxide (DMSO) and methyl iodide (CH_3I) were purchased from Aldrich Chemical Company.

2.2. Preparation and characterisation of hemicelluloses

Isolation of hemicelluloses was performed using a new alkaline hydrogen peroxide method, as follows: to 100 g of finely powered wheat straw was added 1 l of de-ionised water with 0.2% (w/v) Na_2–EDTA·$2H_2O$ (ethylenediamine tetraacetic acid, disodium salt, dihydrate) at pH 6, heated to 90°C for 1 h. The straw was filtered, and washed with de-ionised water. The treatment was repeated three times to remove transition metal ions (e.g. manganese, copper and iron). The straw was extracted with aqueous 10% potassium hydroxide and stirred at room temperature for 16 h. The extract was filtered, 70 ml of hydrogen peroxide (30% H_20_2) was added into the filtrate, the pH adjusted to 11.5 with acetic acid and stirred at 60°C for 16 h. After the reaction, the temperature was allowed to decrease to 20°C, the mixed solution was acidified to pH 6.0 with acetic acid, and triple volume of 95% ethanol (IMS) added, the mixture was left to stand for hours until the supernatant became clear, then the precipitate was filtered and washed with 70% IMS. The pellet was dried in a stream of air (Fig. 1). The dried hemicelluloses were ground in a mill, to pass a 200 μm sieve and stored in a desiccator until required for analysis and methylation.

Hemicelluloses were analysed for neutral sugars and uronic acids after hydrolysis of 10 mg samples for 2 h at 120°C in 7 ml of 2.0 M trifluoroacetic acid (sealed vials).

Samples were evaporated to dryness and the sugars were then converted to their alditol acetates. The sugar derivatives in dichloromethane were analysed by gas chromatography (GC), and the relative percentages were calculated (Blakeney, Harris, Henry & Stone, 1983). Alkaline nitrobenzene oxidation of residual lignin from the hemicellulosic preparation was performed at 170°C for 3 h. The lignin content in hemicelluloses was calculated to be 2.40 by multiplying the yield of phenolic, obtained by nitrobenzene oxidation (Sun, Fang, Rowlands & Bolton, 1998). Methods of uronic acid analysis, determination of phenolic acids and aldehydes in nitrobenzene oxidation mixtures with high-performance liquid chromatography (HPLC), and measurement of the native hemicellulosic molecular weights have been described in previous papers (Lawther, Sun & Banks, 1995; Sun et al., 1996)

IR spectra were obtained on an FT-IR (Nicolet 750) spectrophotometer using a KBr disc containing 1% (w/w) of finely ground sample. The liquid ^{13}C NMR spectrum was obtained on a Bruker 250 AC spectrometer operating at 62.8 MHz, it was recorded at 25°C from 200 mg of sample dissolved in 1.0 ml D_2O. Standard acquisition and processing software were used.

2.3. Methylation of hemicelluloses

The methylation procedure was essentially that described by Hakomori (1964), which is a modification of the method of Sandford and Conrad (1966), which involves the use of the dimethyl sulfinyl anion (Chaykovsky & Corey, 1962) as a base. This was prepared by dissolving sodium hydride (NaH) in dimethyl sulphoxide (DMSO) at 60°C for 45 min. The base was then added to a solution of the polysaccharide in DMSO followed by the addition of methyl iodide (Collins & Ferrier, 1995).

The methylsulfinyl anion was prepared as follows. Into a dry, 100 ml two-necked round-bottom flask fitted with a condenser and a nitrogen (N_2) line containing a magnetic stirring bar was added 1.5 g of hexane-washed sodium hydride. The flask was placed in an oil bath with a thermometer, 15 ml of dried DMSO (Perrin, Armarego & Perrin, 1980; Riddick & Bunger, 1970) was added to the flask and then sodium hydride was added. The flask was heated with stirring under N_2 at 65–70°C (Corey & Chaykovsky, 1962) for 1 h (Furniss, Hannaford, Smith & Tatchell, 1989), until the solution became clear and green and the evolution of H_2 gas ceased.

The methylation method is as follows: wheat straw hemicelluloses were ground to pass through a 200 mesh sieve and dried overnight at 60°C in an oven. Of the dried material, 1 g was added to 50 ml of dry dimethyl sulfoxide in a 100 ml two-necked round-bottom flask containing a magnetic stirring bar, fitted with condenser and N_2 line. The suspension was heated at 120°C and stirred with a magnetic stirrer until all of the hemicellulose dissolved (about 1.5 h) and, after cooling to room temperature, 10 ml of methyl sulfinyl anion was added. The amount of base was a 35% excess over the number of equivalents of hydroxyl plus carboxyl groups present, calculated on the basis of a hemicellulose composed of 78.6% xylose, 14.2% arabinose, 4.8% glucuronic acid and a few percent of other sugars. Upon addition of the anion, a gel formed immediately but gradually liquefied and, after stirring at room temperature for a few minutes (about 10 min), the reaction mixture became homogeneous. The minimum time for complete alkoxide formation after the addition of base was 1–2 h.

For the methylation reaction, the hemicellulose alkoxide solution was maintained at 20°C, and 3 ml of methyl iodide was added to the stirred solution at a rate such that the temperature did not rise above 25°C. Within a few minutes after addition of methyl iodide, heat evolution ceased, the solution became clear and the viscosity was markedly reduced. At this stage, the reaction was deemed complete. The reaction mixture was left overnight with stirring. The reaction mixture was then poured into a 250 ml separator funnel, using 100 ml water for washing, and the mixture was extracted three times with chloroform (1×200 ml, 2×100 ml). The combined extract was washed with water (100 ml). The chloroform extract was concentrated to give a yellow solid (Asensio, 1987) under reduced pressure at 40°C, and the dried sample (1.03 g) was kept in a desiccator for further analysis.

2.4. Determination of methylated hemicelluloses

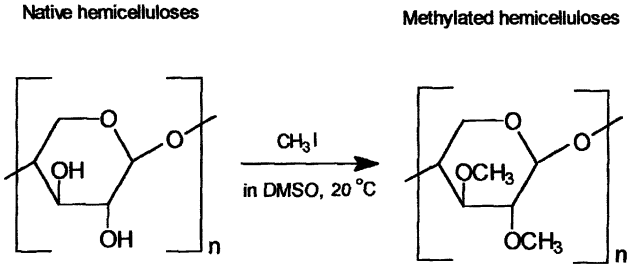
Elemental analysis was used to calculate the DS-value of methylated hemicelluloses. The sample was ground to a powder and dried, then analysed on a Carlo Erba EA 1108 CHN S-O instrument, using the "square to linear fit method" to measure the carbon and hydrogen content in the substituted and native hemicellulose samples. From the carbon and hydrogen contents, the DS-value was calculated.

The thermogravimetry experiments of native and methylated hemicelluloses were conducted using a simultaneous thermal analyser (STA 625). The sample of approximately 10 mg was heated with a heating rate of 10°C/min up to 600°C. Prior to thermal analysis, the samples were dried in a vacuum over 80°C for 24 h.

3. Results and discussion

3.1. Analysis of the isolated hemicelluloses

The isolated hemicelluloses were analysed using GC, GPC, HPLC, FT-IR, and NMR. The GC sugar analysis showed that xylose was present as a predominant sugar component, comprising 78.6% of the total sugars. The second major sugar was arabinose (14.2%); glucose (3.1%), galactose (2.3%), rhamnose (1.4%), and mannose (0.5%) were other minor constituents. The uronic acids, mainly MeGlcA were present in a noticeable amount (4.8%). Gel permeation chromatography (GPC) analysis



Scheme 1.

showed that the native hemicelluloses had an average molecular weight of 21,790 g mol^{-1} with a 1.95 polydispersity, corresponding to a degree of polymerisation of 165. From HPLC analysis, alkaline nitrobenzene oxidation of the lignin content in the isolated wheat straw hemicelluloses indicated a lignin content of 3.86%. The FT-IR and ^{13}C NMR results further confirmed the structural features of the native hemicelluloses, with a backbone of β-(1 → 4)-linked D-Xyl*p* units, side chains with L-Ara*f*, D-Xyl*p* and 4-*O*-D-GlcpA (or D-GlcpA) (Sun et al., 1996).

3.2. Yield and the degree of substitution

The percentage yield of the methylated hemicelluloses was calculated from the mass of product obtained based on the mass of starting material used, and using the following relationship:

$$\% = \frac{\text{Weight of methylated hemicelluloses}}{\text{Weight of native hemicelluloses}/132 \times 160}$$

where 132 is the main chain of xylose unit molecular weight; 160 is the molecular weight of methylated xylose. The weight of the native hemicelluloses was 1 g before methylation. After the reaction, the weight of methylated hemicelluloses was 1.03 g, the theoretical maximum weight of the product was 1.21 g, from these data and the above yield (%) formula calculation, the yield of the product was 85.1%.

The DS of the methylated hemicelluloses is calculated from elemental analysis data, and according to the relationship below:

$$\mathrm{DS} = \frac{\mathrm{C}\%(\mathrm{C_5H_8O_4}) - \mathrm{C_5}}{\mathrm{C} - \mathrm{C}\%(\mathrm{CH_3{-}H})}$$

where C% is from elemental analysis; $C_5H_8O_4$ is the anhydroxylose unit of hemicellulose backbone; CH_3 is the substituent from methyl iodide. Elemental analysis of methylated hemicelluloses gave the following results: C, 51.474%; H, 7.703%; O, 40.823% (the values as calculated from theory are C, 52.49%; H, 7.55%; O, 39.96%). According to the elemental analysis data, the DS-value can be calculated; it was 1.7. This corresponds to an approximate molecular

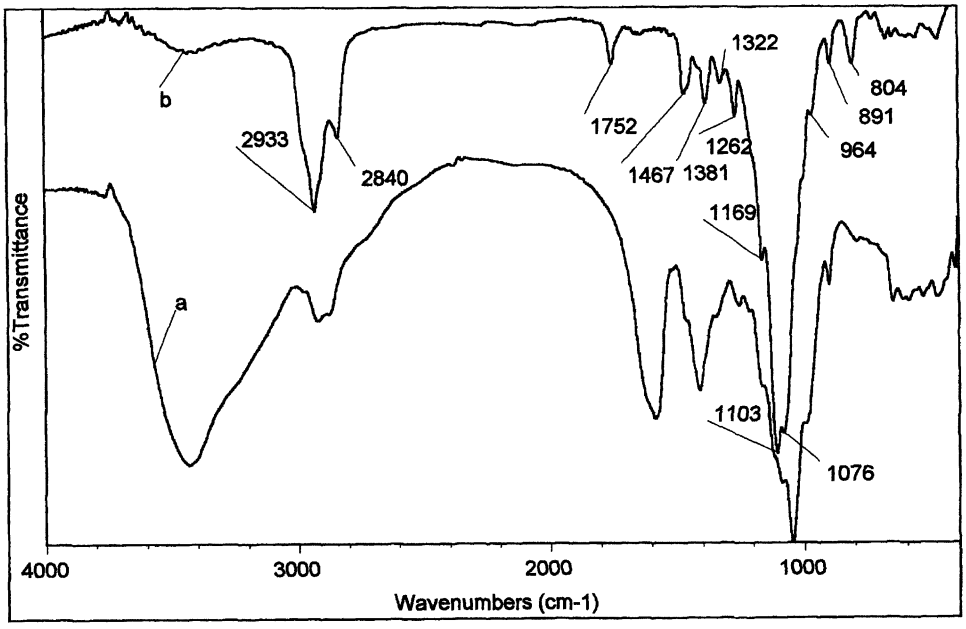


Fig. 2. FT-IR spectra of: (a) wheat straw hemicelluloses and (b) methylated hemicelluloses.

formula (MF) of $C_{6.7}H_{11.9}O_4$ (the theoretical MF is $C_7H_{12}O_4$) for the prepared methylated hemicelluloses.

As can be seen, the yield and DS are satisfactory, which confirms that the method of methylation was successful, over 90% of the free hydroxyl groups in the native hemicelluloses were methylated under the reaction conditions given, but the yield and DS were lower than the theoretical maximum of 100% yield and DS of 2. The incomplete reaction is presumed to be because: (1) some of the hemicelluloses are degraded in the reaction; (2) the hemicelluloses in DMSO may not be fully swollen, in which case the DMSO cannot completely penetrate between the hemicellulose chains and, therefore, some of the reagents do not attack the OH groups of the hemicelluloses. If so, prolongation of the reaction time may be required to ensure complete dissolution of the hemicelluloses in DMSO.

3.3. FT-IR spectra

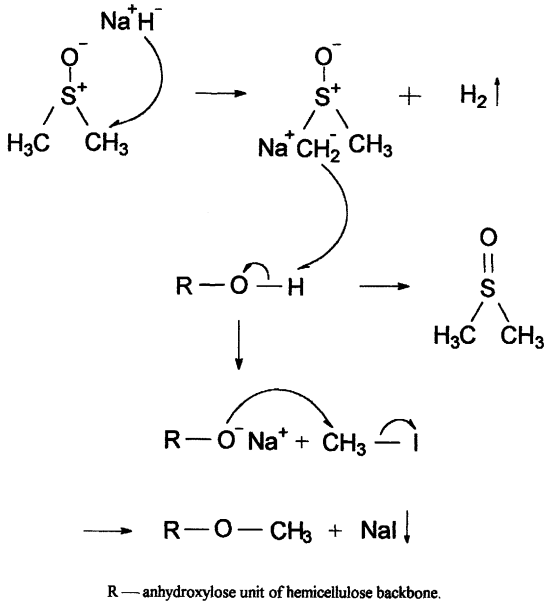
The methylation procedure afforded new material. Scheme 1 (schematic diagram for methylation of wheat straw hemicelluloses) and Fig. 2 show typical analyses of products from methylated and native hemicelluloses. The data illustrate several points: (1) the initial methylation yielded a product with 99% of the theoretical methoxyl content; (2) in the hemicellulosic framework, which contains β-D-xylopyranose units, most of the monomer units bear two hydroxyl groups. Therefore, the maximum theoretical DS-value for the methylated hemicelluloses is 2 (Scheme 1); (3) the uronic acid residues are esterified in the reaction as indicated by the presence of strong carbonyl stretching frequencies identified in the infrared spectrum (b) at 1752 cm^{-1} (ester C=O).

The FT-IR spectra of native hemicelluloses as compared with methylated hemicelluloses are shown in Fig. 2. As can be seen from spectrum (a), the wheat straw hemicelluloses were typical arabinoxylans. The absorbances at 1580, 1467, 1414, 1340, 1255, 1165, 1090, 1043, 990 and 897 cm^{-1} are associated with native hemicelluloses. A sharp band at 897 cm^{-1} is characteristic of β-glucosidic linkages between the sugar units (Gupta, Madan & Bansal, 1987). The low intensity of the band at 990 cm^{-1} suggests the presence of arabinosyl units, which are attached only at position 3 of the xylopyranosyl constituents (Ebringerova, Hromadkova, Alfoldi & Berth, 1992). As the vibrational mode of xylans at 1165 cm^{-1} has been assigned to C–O and C–O–C stretching with some contribution of OH bending mode (Kalutskaya, 1988), the band at 1043 cm^{-1} may be assigned to COH bending modes. The appearance of two other prominent bands at 1414 and 1467 cm^{-1} is attributed to the C–H, OH and CH_2 bending (Kacurakova, Ebringerova, Hirsch & Hromadkova, 1994), respectively. The absorption at 1580 cm^{-1} in spectrum (a) is principally associated with the C=O stretch of carboxylic anion for GlcA in native hemicelluloses. A strong broad band due to hydrogen bond hydroxyl groups appears at 3430 cm^{-1} and the symmetric C–H vibration band appears at 2866 and 2920 cm^{-1} (Aburto, Thiebaud, Alric, Borredon, Bikiaris, Prinos et al., 1997).

From the FT-IR spectra of Fig. 2, there are obvious changes between methylated and native hemicelluloses. In the spectrum of methylated hemicelluloses (b), an absorption band at 1752 cm^{-1}, is attributable to the stretching deformation of the ester carbonyl group. This originates from the 4-*O*-methoxyl group of a glucuronic acid residue in the xylan, which is a small peak in accord with the low uronic acid content, indicating esterification of the uronic acid residues during the reaction. The almost complete disappearance of a peak at 1580 cm^{-1} in spectrum (b) indicates that all of the uronic acid residues have been esterified. In addition, the significant broad band associated with hydroxyl groups (OH) of the native hemicelluloses at 3430 cm^{-1} has clearly reduced in intensity in spectrum (b), after the etherification reaction, owing to ether formation. It thus indicates that the etherification takes place with high DS owing to the OH group peak decreasing substantially. The symmetric C–H vibration band at 2933 and 2840 cm^{-1} has increased, which implies that CH_3 groups have been introduced. In the infrared pattern (b), the bands for CH_3-stretching, CH_3-deformation, and stretching vibrations for the ether bond, particularly for CH_3–O–C at 1169 cm^{-1} were pronounced. Hakomori (1964) assigned bands at 1169, 1103 and 1076 cm^{-1}, due to ether bonds as in spectrum (b) herein. Another change was a pronounced decrease in intensity of the band at 1414 cm^{-1} (CH, OH bending), which indicates that methyl group substitution of the hydroxyl groups present in native hemicelluloses has occurred.

3.4. Methylation mechanism

Classical methylation methods have relied upon the initial conversion of the hydroxyl groups to alkoxides by reacting the polysaccharide with base in aqueous solution (Sandford & Conrad, 1966). The added methylating reagent then reacts with the alkoxides to yield methyl ether. Any free base in the reaction mixture competes with the alkoxide for the alkylating reagent. In the initial reaction, $ROH + B^- \leftrightarrow RO^- + BH$ an equilibrium is established at a point dependent on the strength and concentration of the base, B^- complete conversion to the alkoxide requires a base stronger than OH^-. However, the strongest base that can exist in aqueous solution is the OH^- ion, since stronger bases will react with water to form this ion. Thus, in the standard methylation procedures the extent of ether formation is influenced by the point of equilibrium in the base-catalysed reaction, which in turn is limited by the base strength of OH^-. In the method applied here, these limitations are overcome by use of the strongly basic methylsulfinyl carbanion (Corey & Chaykovsky, 1962) in a non-aqueous medium to generate the polysaccharide alkoxide. It is apparent that the equilibrium in this reaction lies almost completely in the



Scheme 2.

direction of alkoxide formation since, upon addition of the alkylating reagent, formation of the methyl ether is complete within a few minutes. The competing reaction between the excess methylsulfinyl anion and methyl iodide does not interfere as long as methyl iodide is added in excess of total base. Generation of the alkoxide requires about 1–2 h.

The overall chemical reaction was divided into two steps, as shown below:

(1) Hemicelluloses–OH + CH_3–SO–$CH_2^-Na^+$ → Hemicelluloses–O–Na^+ + CH_3–SO–CH_3

(2) Hemicellulose–O–Na^+ + CH_3I → Hemicellulose–O–CH_3 + NaI

The reaction mechanism involves the methyl sulfinyl anion abstracting a proton from the hemicelluloses to afford the polyalcoxide (Scheme 2 — mechanism of methylation of wheat straw hemicelluloses). The stoichiometric methylation reaction requires complete dissolution of the hemicellulose prior to addition of the methylsulfinyl anion, a condition which is greatly facilitated by lyophilisation and sieving of the hemicellulose before attempting to dissolve it in dimethyl sulfoxide.

3.5. ^{13}C NMR spectra

In order to characterise the structural features of hemicelluloses, the isolated hemicelluloses were analysed by ^{13}C NMR spectroscopy in D_2O. The spectrum is shown in Fig. 3, it was interpreted on the basis of reported data for structurally defined L-arabino-(4-*O*-methyl-D-glucurono)-D-xylan (Sun et al., 1996). This D-xylan type of polysaccharide is generally found in the cell walls of wheat straw. Such polysaccharides are based on the structure comprising β-(1 → 4)-linked D-xylopyranosyl residues with some hydroxyl groups substituted with carbohydrate moieties. These

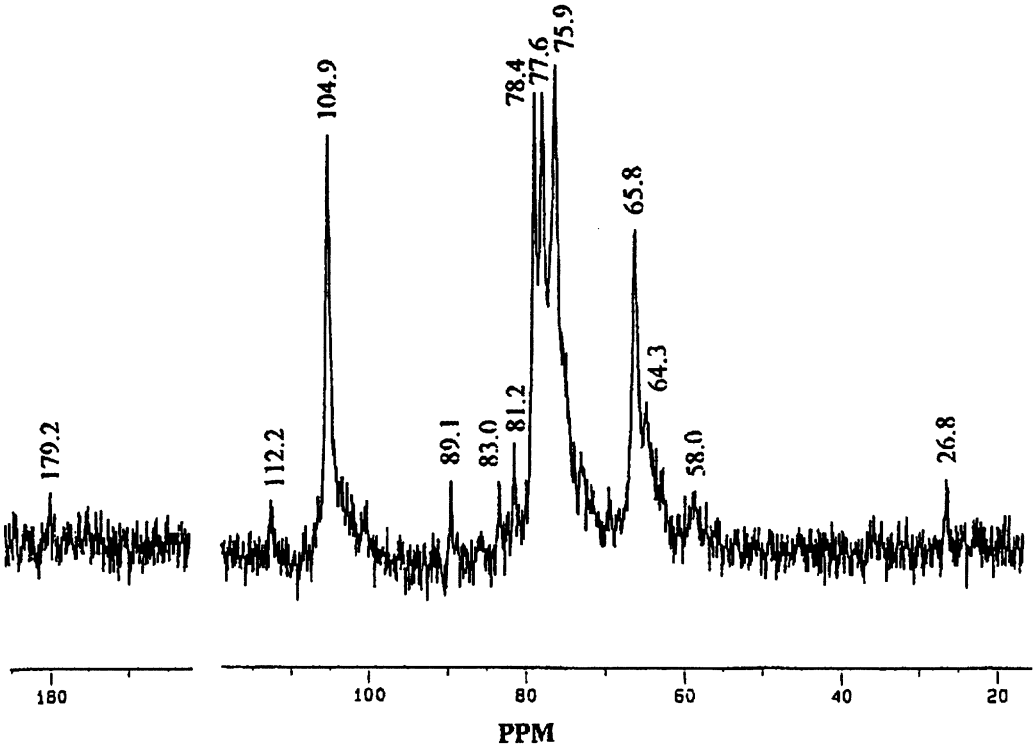


Fig. 3. ^{13}C NMR spectrum of wheat straw hemicelluloses in D_2O.

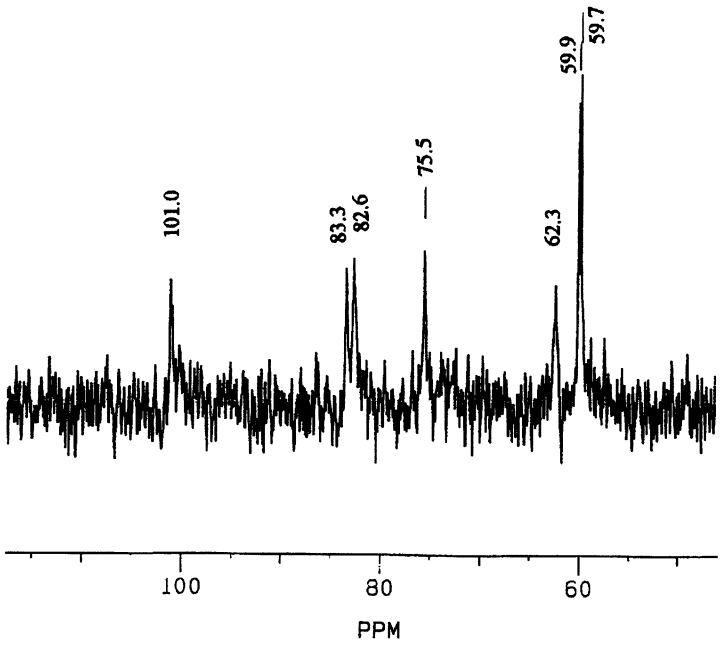


Fig. 4. ^{13}C NMR spectrum of methylated hemicelluloses in D_6-DMSO.

are represented mostly by D-glucuronic acid and its 4-*O*-methyl derivative and L-arabinofuranosyl units. A greater variety of glycosyl substituents is typical of heteroxylans (Kacurakova et al., 1994). In native hemicelluloses Fig. 3, the main β-(1 → 4)-linked D-Xyl*p* units are characterised by the signals at 104.9, 78.4, 77.6, 75.9 and 65.8 ppm, which correspond to C-1, C-4, C-3, C-2 and C-5 of the β-D-Xyl*p* units, respectively (Fidalgo, Terron, Martinez, Gonzalez, Gonzalez-Vila & Galletti, 1993). The signals at 112.2, 89.1, 83.0, 81.2 and 64.3 ppm correspond to C-1, C-4, C-2, C-3 and C-5 of α-L-Ara*f* residue, respectively. Three signals at 176.1, 85.0 (data not shown in the spectrum), and 58.0 ppm originate from the C-6, C-4 and 4-*O*-methoxyl group of glucuronic acid residue in the xylan, which are very weak and in accord with the low uronic acid content. The signal at 26.8 ppm is most likely due to $-CH_3$ from acetic acid from the extraction process, and the corresponding signal at 179.2 ppm is probably due to the carbonyl group of CH_3COOH present within the sample.

Methylation of the hemicelluloses gave a product, which was analysed using solution ^1H NMR and ^{13}C NMR spectroscopy. 30 mg of sample was dissolved in 1.0 ml D_6-DMSO. The spectrum is shown in Fig. 4, from ^{13}C NMR data, the chemical shifts for the main (1 → 4)-linked β-D-Xyl*p* units are characterised by the signals at 101.0, 75.5, 82.6, 83.3 and 62.1 ppm, which correspond to C-1, C-2, C-3, C-4 and C-5 of the β-D-Xyl*p* units, respectively. The strong signals at 59.7 and 59.9 ppm are possibly due to the methyl group ($-CH_3$) substituted on the C-2 and C-3 positions.

3.6. Thermal properties

Thermal characteristics of the native and methylated hemicelluloses obtained were studied using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). As can be seen from the TG plot of native hemicelluloses in Fig. 5a, there is a very slight mass loss until a temperature of 190°C is reached. On further heating there is a sharp weight loss, to give a residue of 40% at 600°C. The DSC (Fig. 5a) curve shows two peaks, the main peak at 285°C, and a small peak at 350°C for this degradation to a carbonaceous residue. In the case of the methylated hemicelluloses, decomposition commences at 230°C with a steady loss continuing with an increase in temperature up to 600°C, when almost 88% of the material is lost in Fig. 5b, and the DSC plot showed a small peak at 240°C together with the main peak shifted towards higher temperature 360°C. Such behaviour might be expected, because the major part of the original material has been converted into a new form (Aggarwal & Dollimore, 1998). Compared with TG plots from Fig. 5, the plots clearly show the presence of the methylated material distinct from the native one by degradation at higher temperature. The greater thermal stability of ether is probably due to the lower amount of remaining hydroxyl groups after methylation.

4. Conclusions

The development of the methylation reaction makes feasible the use of methyl iodide as the alkylating reagent. The present method has obvious advantages in that the reaction is more rapid and complete when catalysed by the carbanion, can be controlled by the amount of the reagent added and can be carried out at room temperature

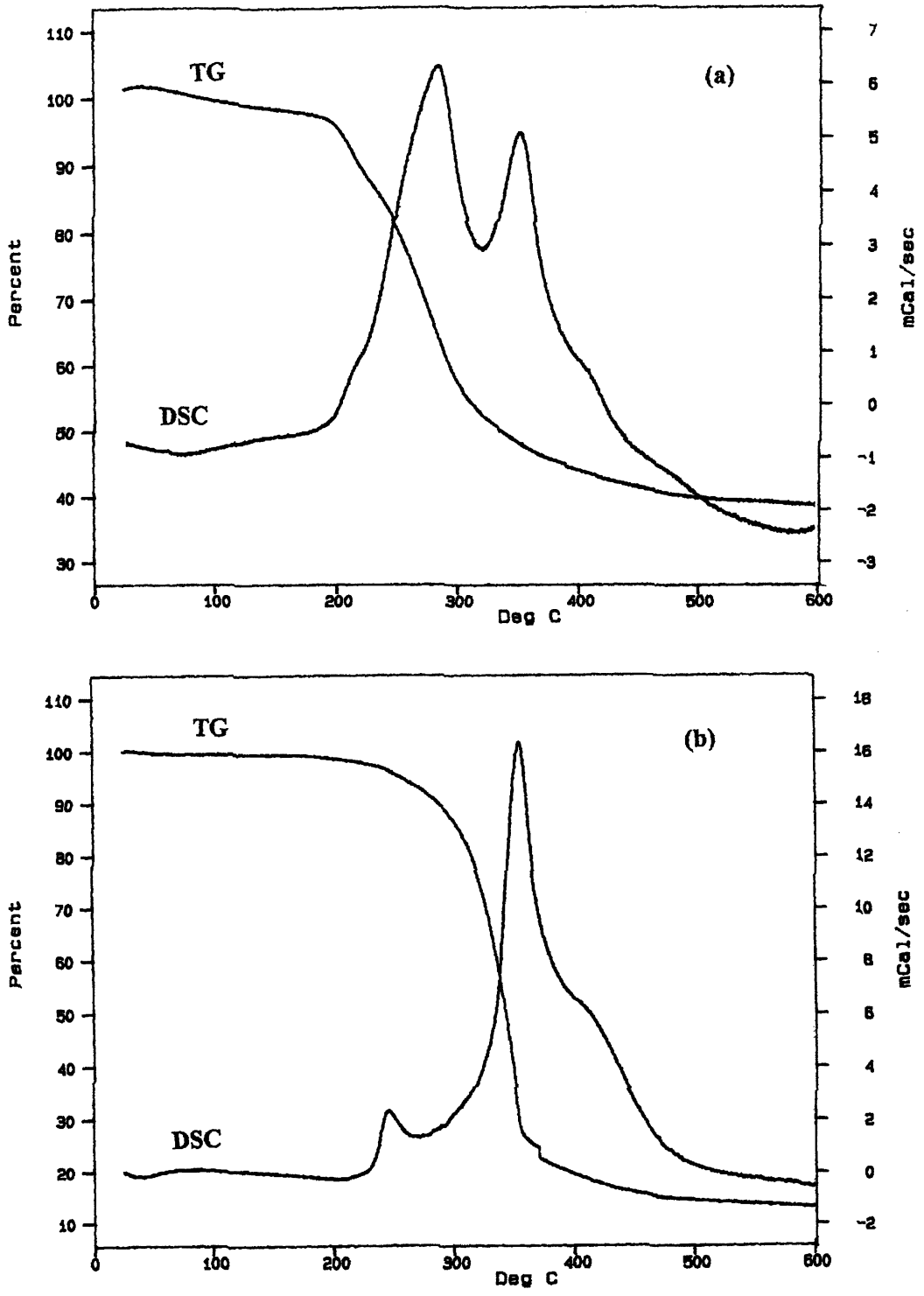


Fig. 5. Thermogram of: (a) native hemicelluloses and (b) methylated hemicelluloses.

in one continuous process without the use of complicated apparatus.

The hemicelluloses studied were successfully etherified using methyl iodide in DMSO with NaH. The structure of the methylated hemicelluloses formed was determined by FT-IR, and further confirmed using solution-state NMR spectroscopy. The carbon content obtained from elemental analysis data permitted calculation of the DS. The native and etherified hemicelluloses were then treated to thermal analysis, the TG-DSC plots clearly show that the etherified

hemicelluloses differ from the native one by the occurrence of the peaks and different decomposition temperatures. In all cases, the TG-DSC shows an endothermic degradation to carbon but, generally, the carbon residue decreases after etherification. The TG plot also demonstrates a marked increase in thermal stability because large amounts of methyl group substituents remain by methylation.

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