

COMMUNICATIONS FROM RESEARCH GROUPS:
CHEMICAL DERIVATISATION OF CELLULOSIC RESIDUES –
1. SULPHOALKYLATION OF HEMICELLULOSES

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INTRODUCTION

In recent years the management of energy and resources generally, in addition to ecological problems, has emphasised the importance of increasing the efficiency of utilisation of resources and improving the protection of the environment. Hemicelluloses constitute a vast resource of renewable raw materials whose use is limited in comparison to their widescale availability. In the present work we have derivatised hemicelluloses extracted from dissolving hardwood pulps to yield sulphonic acid derivatives. These products can be used for analytical purposes as chromatographic supports and in other applications, such as papers, textiles, paints, cosmetics, and as viscosity modifiers. Their suitability in different industries seems due to their compatibility with different ions, their resistance to enzymic attack and their stability at different conditions of pH and temperature (ACS, 1979; Schweiger, 1970).

EXPERIMENTAL

Materials

Twenty-four per cent NaOH hemicellulose solution was kindly supplied by Snia Viscosa. Hemicellulose recovery was carried out by:

- (a) precipitation with 95% ethanol (1:3) at room temperature. The precipitate was dialysed against water and exchanged with ethanol, methanol and ether; finally it was dried under vacuum.

- (b) Gel-like precipitation with DMSO followed by the removal of the aqueous alkaline layer. The treatment with DMSO was repeated several times without drying.

The preparation of dimethylsulphinyllcarbanion (dimsyl) was carried out as reported by Dolle *et al.* (1970); its concentration, determined by 0.5 M acetanilide and 0.1 M triphenylmethane as indicator, was 2.1 mM. 3-Hydroxy-1-propane-sulphonic acid γ -lactone (propane sultone) was purchased by SIGMA. DMSO was dried by distillation over calcium hydride immediately prior to use.

Derivatisation Reaction

To a suspension of hemicelluloses (2 g) in DMSO (50 ml) different amounts of dimsyl were added (10–100 ml). The suspension was stirred (450 r.p.m.) at $25 \pm 0.1^\circ\text{C}$ for 5 min–4 h under a nitrogen atmosphere. The unreacted dimsyl was removed by centrifugation and several washings with DMSO under a stream of nitrogen. The product was suspended again in 20 ml DMSO and 2.0–100.0 mmol/g hemicellulose of propane sultone in 10 ml DMSO were added. The reaction was carried out while stirring at $25 \pm 0.1^\circ\text{C}$ for 16 h under nitrogen atmosphere. The mixture was poured into 100 ml acetone and neutralised with acetic acid. The precipitate was washed with methanol, dried under vacuum and then dissolved in water and eluted from a column of Sephadex G-15 with water to eliminate reaction by-products.

Determination of Content of SO_3^- Groups

The SO_3^- content of the sulphopropylated hemicelluloses was determined by conductimetric titration with 0.1 N NaOH as reported by Casu & Gennaro (1975) for heparin and other mucopolysaccharides.

NMR Spectra

The ^1H NMR spectra were recorded at 90 MHz on a Perkin Elmer R 32 spectrometer. The spectra were obtained at 90°C , using deuterium oxide as solvent and 3-trimethylsilylpropionic acid sodium salt (TSP) as internal reference.

The ^{13}C NMR spectra were recorded on a Varian CFT 20 (20 MHz) instrument with coupling using a gated ^1H decoupler sequence to retain nuclear Overhauser enhancement. Methanol was used as the internal reference and deuterium oxide as solvent.

RESULTS AND DISCUSSION

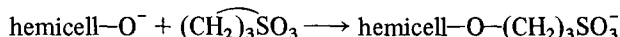
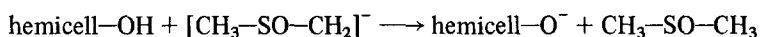
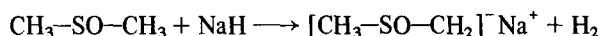
The sulphonation or sulphatation of polysaccharides has previously been carried out in heterogeneous phase on substrates, like cellulose, completely insoluble in the reaction medium (Bischoff *et al.*, 1973; Natus & Goethals, 1968; Schweiger, 1972a) or on substrates, like glucuronons, in which the extensive formation of hydrogen bonds between hydroxyl groups prevents complete solubilisation and is responsible

for their lack of reactivity (Schweiger, 1972*b*). More recently, methods of derivatising polysaccharides in homogeneous or gel-like phase have been proposed (Nicholson & Johnson, 1977; Rinaudo *et al.*, 1972; Schweiger, 1979) but some of these have resulted in degradation of the substrate (Bischoff *et al.*, 1973).

In this work the sulphonation reaction has been carried out on hemicelluloses previously activated by changing their morphology in order to enhance the inner surface and thus their accessibility to the chemical agents (Guirely, 1979; Philipp, 1980*a,b*; Yoon Lee *et al.*, 1975).

Two approaches have been used: in the first the recovery of the hemicelluloses from their alkaline solutions is accomplished by precipitation with ethanol (hemicelluloses (a)). The hydrogen bond reformation is reduced by solvent exchange thereby rendering the hydroxide groups available for reaction. The second method involves a gel-like precipitation with suitable amounts of DMSO which is, as a matter of fact, the solvent used in the derivatisation reaction (hemicelluloses (b)).

The hemicelluloses are pretreated with dimsyl to enhance their reactivity and to locate the active reaction centres on the macromolecules without consumption of the esterifying agent by secondary reactions:



The derivatisation reaction conditions have been studied as a function of dimsyl/hemicellulose ratio (Fig. 1), pretreatment time with dimsyl (Fig. 2) and propane

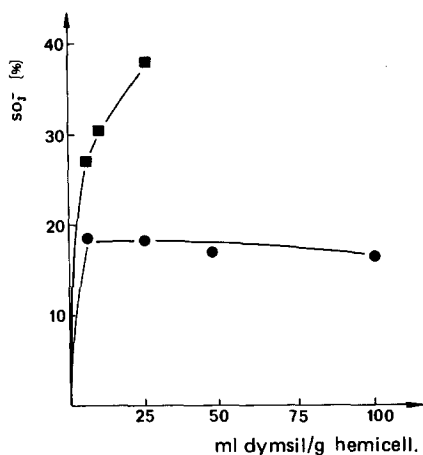


Fig. 1. Influence of dimsyl/hemicellulose ratios on SO_3^- content of hemicellulose. •, Hemicelluloses (a); ■, hemicelluloses (b). Conditions: $(\text{CH}_2)_3\text{SO}_3$ concentration 18 mmol/g hemicellulose; reaction time 1 h.

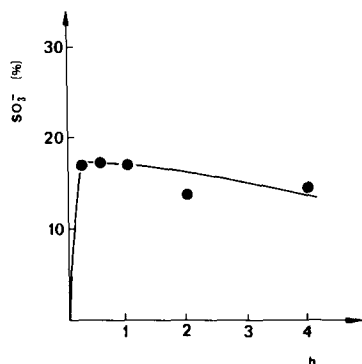


Fig. 2. SO_3^- content as function of dimsyl treatment time. Conditions: 25 ml dimsyl/g hemicellulose; 18 mmol $(\text{CH}_2)_3\text{SO}_3$ /g hemicellulose.

sultone/hemicellulose ratio (Fig. 3) using hemicelluloses activated in two different ways. A dimsyl/hemicellulose ratio of 25 ml/g gives the highest content in SO_3^- groups for the hemicelluloses (b); for the hemicelluloses (a) the highest SO_3^- content is achieved by a lower quantity of dimsyl, but the yield is significantly lower.

The influence of the treatment time with dimsyl has been studied only for the hemicelluloses (a) (Fig. 2). Treatment times between 15 and 30 min are sufficient to obtain the highest yield.

Figure 3 shows the influence of the propane sultone/hemicellulose ratio using hemicelluloses activated in the two different ways.

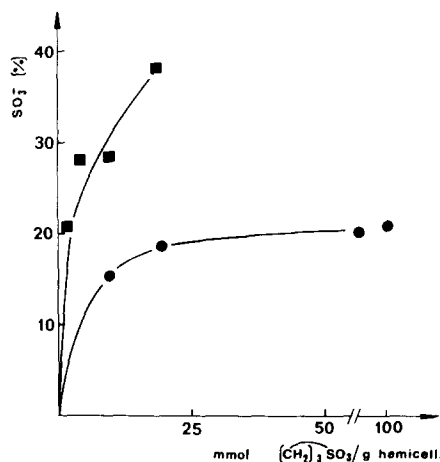


Fig. 3. Influence of propane sultone concentration on SO_3^- content. ●, Hemicellulose (a); ■, hemicellulose (b). Conditions: dimsyl concentration 25 ml/g hemicellulose; dimsyl reaction time 1 h.

A continuous increase of SO_3^- content is observed for hemicelluloses (a) whilst for hemicelluloses (b) an immediate increase in SO_3^- groups is observed at low values of propane sulfone/hemicellulose ratio.

A preliminary spectroscopic investigation of sulphopropylated hemicelluloses has been carried out by ^1H and ^{13}C NMR. The spectra of the unmodified hemicellulose substantially correspond to those of the xylans. The backbone heterogeneity due to non-uniform substitution caused a greater complexity of the signal in the anomeric proton region (about 4.7 ppm) of the ^1H spectra.

The sulphopropyl substituent signals were observed at 2.05 and 2.95 ppm for the CH_2 and $\text{CH}_2\text{—S}$ protons, respectively. The O—CH_2 signal at about 3.6 ppm fell in the region of H-2, H-3 and H-5 of the xylopyranose ring. The degree of substitution was determined from the area ratio of the anomeric and methylenic proton signals. The results were fairly consistent with those obtained by conductimetric titration.

Upon sulphopropylation, the ^{13}C spectra of the hemicelluloses show extra signals due to the sulphopropyl substituents (at 27.79 and 50.94 ppm) as well as to substituted C-2 and C-3 in the 82–85 ppm region. Signals of unsubstituted carbons show either decreased intensity or (as for C-1) significant broadening.

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