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Quaternized xylans: synthesis and structural characterization

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Quaternization xylans were prepared by treating xylans differing in structural and molecular properties with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHMAC) in aqueous NaOH under mild reaction conditions. The degree of substitution with quaternary ammonium groups can be monitored by altering the amount of CHMAC at optimum molar ratios of NaOH/CHMAC in the range 1·2–1·6, without changing the structure of the xylan backbones. Hot water pretreatment of the xylans in the alkaline activation step significantly enhances their reactivity. The presence of alkylammonium substituents was revealed by IR and NMR spectroscopy. The applicability of quaternized xylans as a retention aid in papermaking is demonstrated on thermomechanical pulp. Xylans, therefore, represent an important renewable resource for the production of novel cationic biopolymers.

INTRODUCTION

Due to the shortage of liquid fuel reserves and the growth of ecological problems, there is a need to increase the efficiency of biomass utilization and for new biodegradable polymers. From this point of view, xylans, which are next to cellulose the most abundant plant polysaccharides, are important (Whistler & Shah, 1978; Stscherbina & Philipp, 1991; Ebringerová, 1992). Though widely distributed in hardwoods and annual plants, their use is up to date limited mainly due to structural diversity, depending on botanical origin and isolation procedure (Wilkie, 1979; Aspinall, 1983). Most xylans are strongly hydrogen-bonded and consequently insoluble in water, which also limits their utilization.

Modification is useful to add or modify functionality. Quaternization of xylans enhances their solubility and yields cationic or ampholytic polymers which have similar chemical properties to quaternized derivatives obtained from starch, galactomannan, cellulose, cyclodextrin and chitosan (Käufer *et al.*, 1980; Muzzarelli & Tanfani, 1985; Domard *et al.*, 1986; Ito *et al.*, 1986; Deratani *et al.*, 1989; Loubaki *et al.*, 1991). Therefore, they may find various technical and medical applications. The first report on cationization of hemicelluloses isolated from pulps (Pulkkinen *et al.*, 1973) concerns the preparation of flocculants and adhesives. Cationic hemicelluloses, which are useful as beater additives (Antal *et al.*, 1991), have been extracted from quaternized hardwood metal (Ebringerová *et al.*, 1987).

In this study, quaternized polysaccharides were prepared from heteroxylan models differing in structural and molecular properties, and the preparation conditions, degree of substitution and structural features of the derivatives were examined.

EXPERIMENTAL

Samples

The heteroxylan models (listed in Table 1) were prepared on a semitechnical scale from beechwood (GX) (Eberingerová & Toman, 1986), corn cobs (AGX) (Ebringerová *et al.*, 1988) and its water-soluble (AGX-S) and water-insoluble (AGX-IS) fractions, and from rye bran (AX) (Hromádková & Ebringerová, 1987). Xylan-GXL, the byproduct of cellulose fibre production (Lenz *et al.*, 1984), was kindly supplied by Lenzing AG (Austria). The 60% aqueous solution of 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHMAC) was purchased from Fluka.

Table 1. Analytical characteristics of model nonmodified xylans

Xylan type	Plant source	Sugar composition					$[\eta]$[b] (dl/g)	DS_0[c]	Solubility in water (%)
		Ara	Xyl	Glc (Rel. wt. %)	Gal	GA[a]			
GX	Beech wood	0	81·1	2·0	0·5	16·4	0·42	0·13	c. 80
GXL	Beech pulp	0	92·5	3·6	0·2	3·7	0·28	0·03	Insoluble
AGX-N	Corn cob	2·3	87·5	2·9	3·4	3·9	0·86	0·06	Insoluble
AGX-S	Corn cob	13·2	74·5	1·0	2··7	8·6	0·76	0·25	100
AX	Rye bran	12·0	85·9	2·1	0	tr	2·65	0·14	Insoluble

[a] Calculated as Na^+ salt of the 4-*O*-methyl-D-glucuronic acid unit, $M_r = 213$.
[b] Measured in dimethyl sulphoxide (DMSO) (Lebel & Goring, 1963).
[c] Degree of substitution (branching) of the xylan chain expressed as moles of glycosyl units (Ara and/or GA) per xylose unit.

Analyses

The degree of substitution (quaternization, DSQ) of the trimethylammonium-2-hydroxypropyl (TMAHP) xylan in its OH^- form has been analysed using a Perkin-Elmer Elemental Analyzer Model 240. DSQ was expressed as moles of TMAHP groups per xylose unit and calculated from the nitrogen content according to the equation: $DSQ = 9{\cdot}43 \times \%N/(100-\%A-9{\cdot}57\%N)$, where %A represents the sum of the contents of arabinose and 4-*O*-methylglucuronic acid units of the parent xylan (according to the data in Table 1).

^{13}C-NMR spectra (75·468 MHz) were recorded with a FT-NMR spectrometer (Bruker AM-300) at 40°C for solutions in D_2O (internal methanol, 50·15 ppm relative to Me_4Si) and DMSO-d_6. For the identification of CH_2 groups, the DEPT sequence was used from the standard Bruker software library. IR spectra were measured in KBr pellets (2 mg sample/200 mg KBr) prepared by the standard technique and recorded with a Perkin-Emer G 983 spectrophotometer operating at 4 cm^{-1} resolution and equipped with a data station DS 3700. The peak absorbance ratio method has been applied to the spectra with baseline at 800 and 1520 cm^{-1}.

Etherification of xylans

To 1 g of a xylan sample, an aqueous solution of NaOH (17·5 or 10%, see Table 2 and Fig. 1) was added, and the mixture was stirred at 20°C for 0·5 h. Various amounts of CHMAC were then added under intensive stirring at 22°C for 20 h. The reaction produce was in one experiment dialysed for 48 h against distilled water and the nondialysable portion was freeze-dried. In all other experiments, the reaction product was poured into four volumes of acidified (1% HCl) ethanol and the precipitate was washed with four volumes of 80% ethanol. It was then dispersed in distilled water, dialysed until free of chloride ions, and recovered by lyophilization. In the experiments with hot water pretreatment, the xylan was dispersed in distilled water and heated to 95°C for 15 min. After cooling to 20°C, 660 g/litre

Table 2. Quaternization of xylans in relation to the molar ratios of reactants

Xylan	Molar ratios		N (%)	DSQ	DS[c]	Yield[d] (g/g)
	CHMAC/Xyl[a]	NaOH[b]/CHMAC				
GX	1·00	0·80	0·82	0·10	0·09	0·72
	1·00	1·20	3·42	0·59	0·51	1·14
	1·00	1·40	3·07	0·50	0·44	1·05
	1·00	2·00	2·27	0·34	0·29	0·98
	1·00	4·10	0·98	0·12	0·10	0·78
GXL	4·00	0·80	1·33	0·15	0·14	1·01
	4·00	1·10	2·06	0·26	0·25	1·17
	4·00	1·60	3·27	0·49	0·46	1·32
	4·00	2·10	2·08	0·37	0·35	1·04
AGX-N	4·00	1·00	2·48	0·28	0·25	1·13
	4·00	1·20	3·10	0·47	0·39	1·29
	7·00	2·00	2·24	0·31	0·28	1·24
	17·00	1·80	2·34	0·33	0·29	1·37

[a] Xylose unit, $M_r = 132$.
[b] Alkaline activation: 17·5% NaOH.
[c] Degree of quaternization related to the total amount of moles of all sugar constituents (based on data in Table 1).
[d] Product weight related to the starting sample weight.

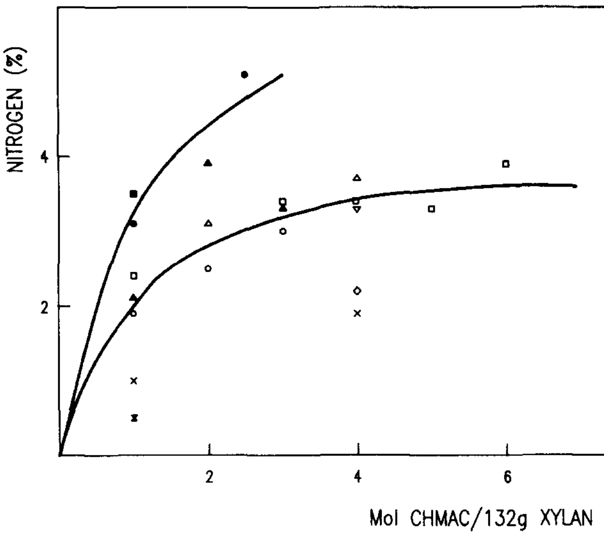

Fig. 1. Degree of quaternization (% N) of TMAHP–xylans as a function of the alkaline activation conditions and CHMAC concentration; 10% NaOH (x); AX (*); 17·5% NaOH, AX (+); GXL (o); GX (□); AGX-N (△); AGX-S (▽). The full symbols stand for the hot water pretreated samples of GXL, GX and AGX-N.

NaOH was added to adjust the concentration of the alkali to 17·5%. The reaction mixture was further treated in the same manner as above. The exchange of the Cl– form into the OH^- form was performed by treating the modified xylan with excess of 1 M NaOH at 10°C for 1 h, followed by removal of alkali by dialysis. The derivatives were stored in the Cl^- form, obtained after neutralization to pH 7 with 0·05 M NaOH.

Retention test

To 500 ml of a 0·5% aqueous suspension of thermomechanical pulp fibres, up to 1% (based on pulp) of TMAHP–xylan dissolved in distilled water was added and the mixture was intensively stirred for 10 min; then, 100 ml of the suspension was taken from the bottom of the beaker. After sedimentation for 24 h, the upper part was decanted and used for turbidity measurement. The sedimented suspension was filtered through filter paper, dried at 105°C for 4 h and weighed. The retention of fibres was calculated according to the equation:

$$\text{Retention } (\%) = [1 - (w_1 - w_o)/0{\cdot}5] \times 100$$

where w_1 is the weight of filter paper with retained fibres, and w_0 is the weight of filter paper.

RESULTS AND DISCUSSION

The synthesis of quaternized xylans followed the same general outline as the preparation of other cationic polysaccharides, namely, activation by alkalization to generate high nucleophilic reactivity and to increase the accessibility of the polysaccharide ultrastructure, particularly of the water-insoluble samples, followed by the etherification step. Similarly, as in the case of celulose (Antal & Kuniak, 1980), the 17·5% aqueous NaOH was found to be the most suitable alkali used for activation. As seen in Fig. 1, at lower NaOH concentration, the degree of substitution expressed as %N decreased probably due to preferential oxirane ring hydrolysis. At NaOH concentrations higher than 17·5%, lower degrees of substitution were obtained (Anthal, 1977: Käufer *et al.*, 1980) due to suppression of the oxirane ring opening of the reactive 2,3-epoxypropyltrimethylammonium chloride intermediate formed from CHMAC. As seen from Table 2, the DSQ is strongly influenced by the molar ratio NaOH/CHMAC. For the different xylans and CHMAC/Xyl ratios, there is an optimum range between 1·2 and 1·6. This value was 1·2 for microcrystalline cellulose (Antal & Micko, 1992), whereas in the case of wood meal, a higher value (1·8) was found, caused by the consumption of alkali by lignin carboxyl and acetyl groups (Antal *et al.*, 1984). The reaction product yield shows the same trend as DSQ. At higher NaOH/CHMAC ratios, side reactions of the etherifying agent are favoured and DSQ decreases. At lower ratios, the lower values are due to an insufficiency of NaOH in the reaction medium (Antal, 1977).

The extensive formation of hydrogen bonds in xylans, particularly in the low-branched types, during isolation and drying (Kačuráková, 1992), results in partial solubility or even insolubility of the polymers in water and decreases the reactivity of hydroxyl groups towards alkylation. Therefore, the most important step in xylan quaternization is the alkaline activation with 17·5% NaOH. Preswelling of the xylan in hot water, followed by addition of the appropriate amount of strong alkali to adjust the required 17·5% concentration, was shown to yield a higher level of substitution at the same amount of added CHMAC (Fig. 1). The pretreatment facilitates the rapid conversion of the xylan into a more uniform gel, whereas under the direct alkalization conditions, only the outer parts of the xylan particles are highly swollen in contact with the limited amount of added alkali. Consequently, the diffusion of the reactants into the inside of particles is retarded. Similarly, a higher DSQ and more uniform substitution was also achieved when other xylan derivatization reactions had been performed in a gel-like phase (Focher *et al.*, 1989; Philipp *et al.*, 1987).

In Fig. 1, a progressive increase of the nitrogen content of TMAHP–xylans, with increasing amounts of added CHMAC in the optimum NaOH/CHMAC ratios range, is seen. The quaternization levels off at *c.* 5% N, corresponding to a DSQ of *c.* 1·0, which represents a fairly high substitution level. As seen in Table 2, the degree of substitution (DS) related to all sugar constituents, not only to the xylosyl ones, is lower, depending on the composition of the unmodified xylans. In spite of a larger excess of added CHMAC, the DSQ show no increasing tendency (Fig. 1, Table 2). The high NaOH/Xyl ratio as well as the nonoptimized reaction temperature/time conditions may contribute to this result.

Due to strong electrostatic interactions between the quaternary ammonium substituents and ionized polysaccharide hydroxyl and carboxyl groups in alkaline medium, the incomplete removal of degradation products may give a falsely high value of DSQ of the TMAHP derivative calculated from the nitrogen content. Therefore, two separation methods were compared on the basis of ^{13}C-NMR spectroscopy.

As seen in Fig. 2, the ^{13}C-NMR spectrum of the nondialysable portion of the reaction product (TMAHP-AGX, 4·6% N) contains new strong signals at δ 67–69, 63 and 53·5–55·5, assigned by the DEPT method to carbon resonances of the CH_2, CHOH and $N^+(CH_3)_3$ groups. These positions correspond to those of the resonances present in the spectrum (Fig. 2, inset) of the alkali-hydrolysed CHMAC. The results indicate that the nitrogen of the quaternized product was mostly bound in degradation products not removed by dialysis. In the ^{13}C-NMR spectrum (Fig. 3) of the TMAHP-

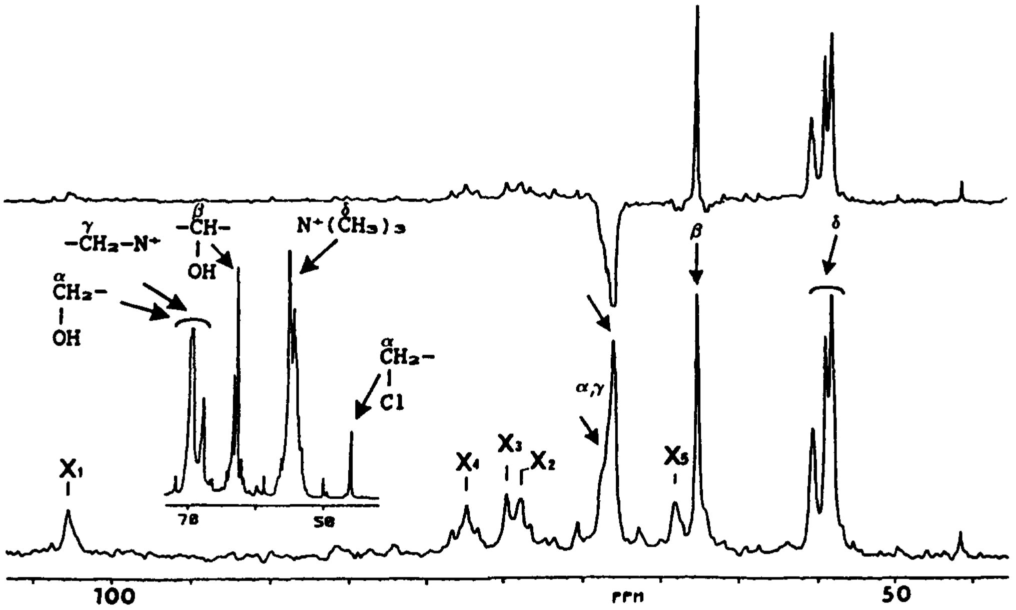

Fig. 2. ^{13}C-NMR spectrum (in D_2O) of TMAHP-AGX (4·6% N) and its DEPT spectrum. Inserted is the spectrum of alkali-hydrolysed CHMAC; $CH_2(X)$-$CH(OH)$-CH_2-N^+-$(CH_3)_3X^-$, where X is Cl or OH.

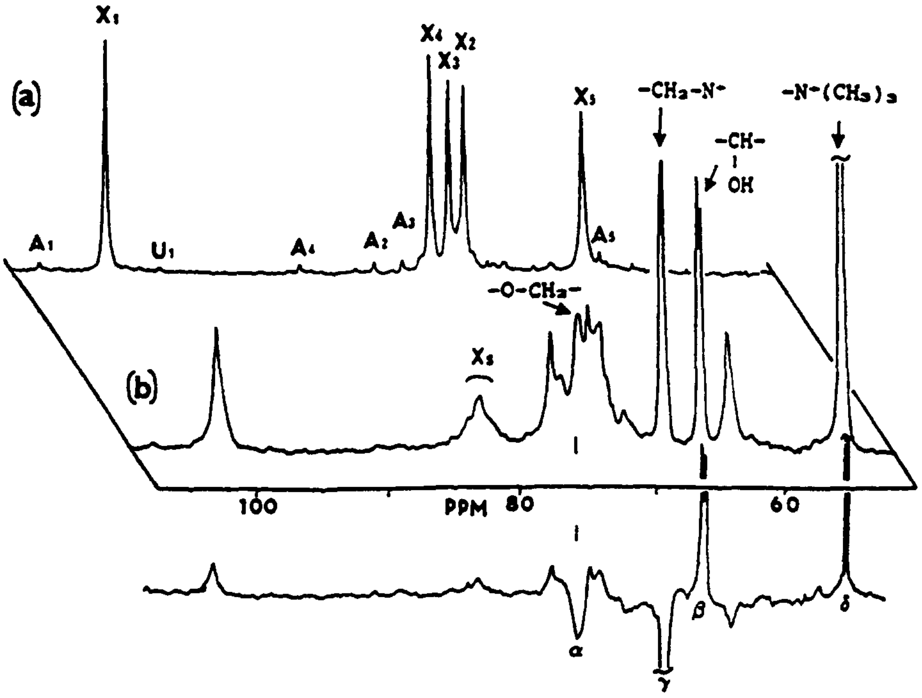

Fig. 3. ^{13}C-NMR spectra of (a) AGX-N in DMSO-d_6, and (b) TMAHP-AGX-N (3·9% N) and its DEPT spectrum, in D_2O.

AGX-N (3·9% N), which was isolated from the reaction medium by acidified ethanol precipitation, there are changes in the number and positions of the strong signals in comparison with data in Fig. 2. The most intensive signal at δ 55·3 is due to Cδ carbons of the quaternary ammonium moiety. The downfield shifted, split signal at δ 66·2–66·4 corresponds to Cβ (CHOH) of the substituent. The DEPT experiment revealed two positions of methylene groups: that of the carbon Cγ (CH_2-N^+) at δ ~ 69·3 and that of the carbon Cα, which is in the α- position to carbons of the xylosyl units and downfield shifted to δ ~ 75·3. This is a proof that the nitrogen was bound to the xylan chain in the form of the TMAHP substituent. Therefore, the second isolation procedure has been employed in all experiments of this study. In the recently reported ^{13}C-NMR spectrum of TMAHP–amylose hydrolysate (Katsura *et al.*, 1992), both Cα and Cγ carbons of the TMAHP substituent were claimed to resonate at δ 62·7–64·2. Obviously, the signal of the Cα at ~ δ 75 being located in the region of C-2/C-5 resonances of glucose was omitted. It can explain the inaccuracy in calculating the TMAHP distribution mentioned by the authors.

Comparing the ^{13}C-NMR spectra of various xylans before and after quaternization (Figs 2–4) it is evident that the primary structural features were not altered during the modification. The intensity of the signals corresponding to Cα–Cδ of the substituent increases with increasing DSQ. However, their intensities are not equal; Cα, being directly attached to the xylan backbone, is least mobile and shows the lowest intensity. A distinct splitting of the Cβ signal with different intensity ratios of the two resonances, as well as a less pronounced splitting of the Cγ signals were found in all TMAHP–xylans. They may reflect different positions of the TMAHP substituent in the xylan molecule and/or two diastereotopic Cβ carbons, as proposed by Loubaki *et al.* (1991).

Due to the expected deshielding effect for an ether substituent (Gorin, 1981), the group of signals at δ 81–85 in the spectra of TMAHP–xylans arises mainly from substitution of the xylose moieties at positions 0–2 and/or 0–3. The resonance at δ ~ 82·7 also prevails at higher substitution levels. This is best demonstrated in the spectra of TMAHP derivatives of the low-branched AGX-N (Fig. 3), because the overlapping of resonances of C-4 of the glucuronosyl units at δ 83·5 and those of C-2/C-4 of the arabinofuranosyl units at ~ δ 81/86 assigned in previous papers (Odonmažig *et al.*, 1990; Ebringerová *et al.*, 1992) is small and decreases with increasing DSQ. Also, the possible substitution of the xylan side-chains is probably for the same reason (not reflected in the NMR spectra of the above mentioned xylan derivatives): their DSQ exceeds several times the degree of branching of the xylan backbone. In the ^{13}C-NMR spectrum of the quaternized highly branched AGX-S (Fig. 5), an additional O—CH_2 signal was detected at δ 73·2. It might originate from a Cα resonance of a new substitution site or the α-shift of 0–5 substituted arabinofuranosyl units.

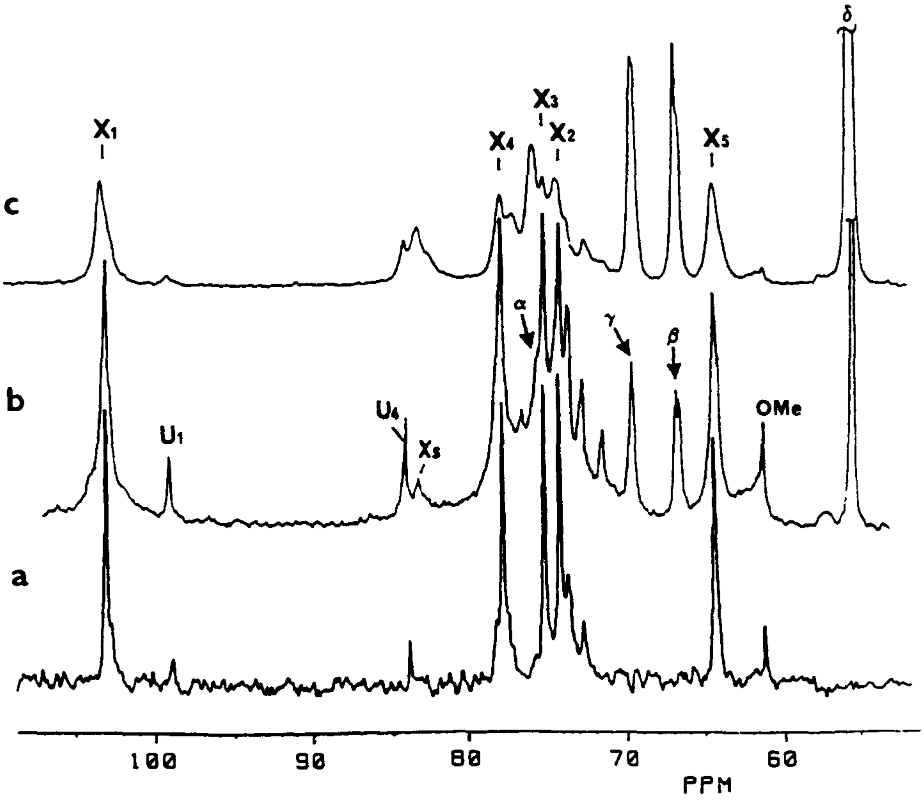

Fig. 4. ^{13}C-NMR spectra (in D_2O) of (a) GX, and TMAHP-GX with (b) DSQ = 0·18 and (c) DSQ = 0·65.

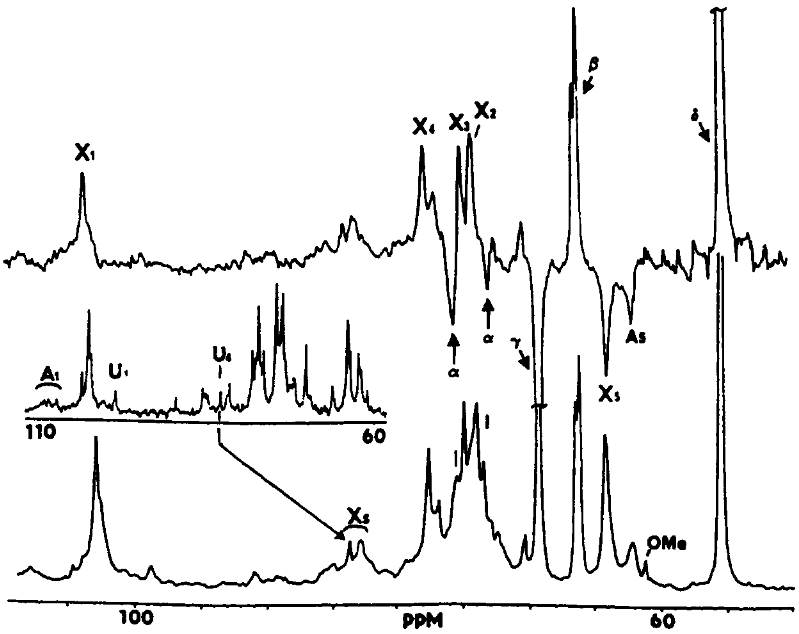

Fig. 5. ^{13}C-NMR spectrum (in D_2O) of TMAHP-AGX-S (DS_Q = 0·55) and its DEPT spectrum (upper curve). Inserted is the ^{13}C-NMR spectrum of the nonmodified AGX-S.

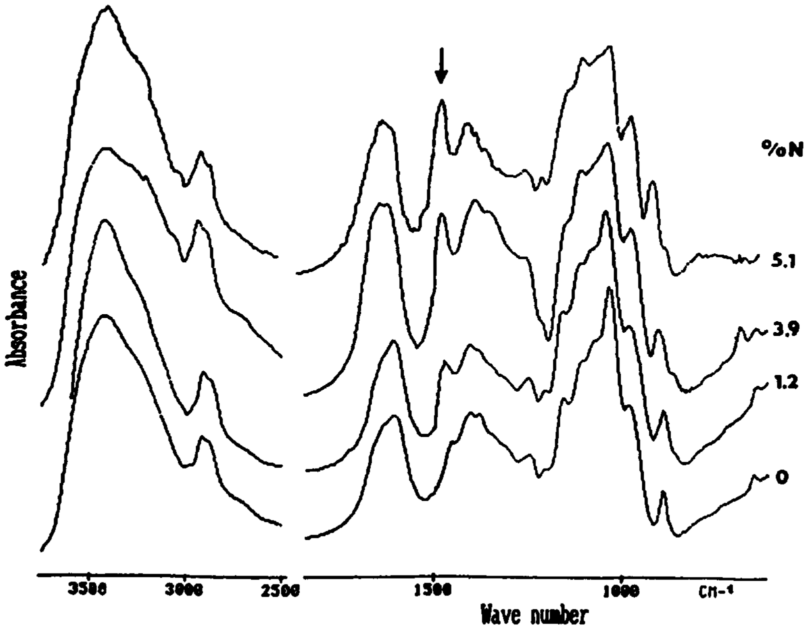

Fig. 6. IR spectra (in KBr) of TMAHP-GX in relation to the nitrogen content (% N).

The most likely source of so many bands in the region δ 81–85 is the nonuniform distribution of the TMAHP substituents in the xylopyranosyl units and/or along the xylan chains. A further study on hydrolysates of TMAHP–xylans is in progress in order to obtain information about the distribution pattern of quaternized xylans.

The IR spectra of the TMAHP–xylans (Fig. 6) show distinct deviations from those of the parent polysaccharides in the OH-stretching region (3400–3100 cm^{-1}) and in the region 1200–900 cm^{-1} where most bands arise from highly coupled C—C, C—O and C—OH stretching modes of the polymer backbone (Marchessault & Liang, 1962). With increasing % N, there is a broadening of many bands and sharpening of the band at 1112 cm^{-1}, attributable to the ring C—O stretching with great contribution of OH bending modes. The regions mentioned are susceptible to changes in the complex hydrogen bond system of the superstructure formed during isolation and drying (Kačuráková, 1992), which is altered by introduction of the positively charged substituents. Simultaneously, a new band appeared at

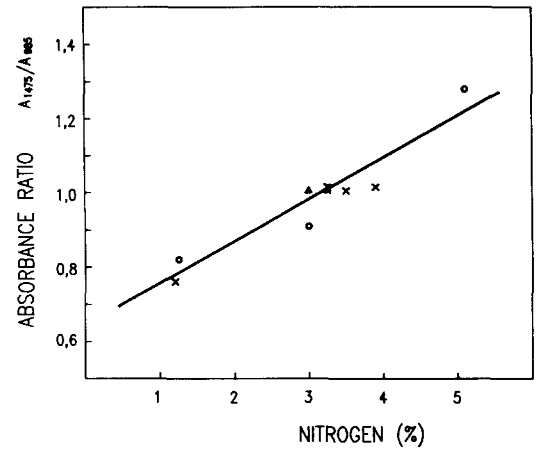

Fig. 7. Correlation between % N of the TMAHP–xylans and the absorbance ratios $A_{1475 cm^{-1}}/A_{985 cm^{-1}}$.

1475 cm^{-1} which can be assigned to CH_2 bending mode and methyl groups of the substituent. A corresponding band at 1470 cm^{-1} was present in the IR spectra of N-substituted TMAHP chitosan (Loubaki *et al.*, 1991). A valid correlation was found between the nitrogen content and the peak absorbance ratio at 1475 cm^{-1}/985 cm^{-1} (Fig. 7), which can be used for detection and quantitative analysis of TMAHP–xylans.

From the results presented it is obvious that the different structural features of the xylans under investigation have no significant influence on the extent of the alkylation reaction, providing that sufficient activation of the polysaccharide is achieved. The result is of practical importance, since xylan mixtures, usually obtained by extraction of xylan-rich materials, could be used in an industrial process.

Due to the presence of cationic groups, TMAHP–xylans were tested as a retention acid in papermaking.

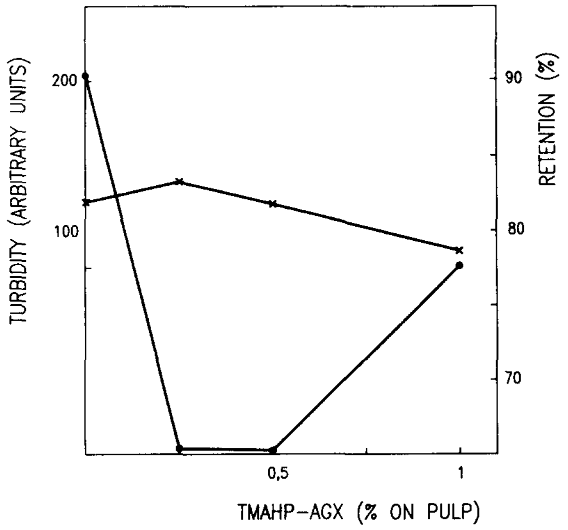

Fig. 8. Retention of thermomechanical pulp fibres and turbidity of spent water in relation to the addition of TMAHP-AGX.

As illustrated in Fig. 8, a small addition (0·25% based on pulp) of TMAHP–AGX to an aqueous dispersion of thermomechanical pulp fibres increases retention by *c.* 3%. The maximum retention corresponds with the minimum of turbidity of the spent water, thus reflecting the flocculating ability of the derivative. The results indicate the potential of quaternized xylans as cationic polymer additives.

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