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^{13}C-N.M.R. SPECTROSCOPIC STUDY OF THE HOMOGENEOUS SULPHATION OF CELLULOSE AND XYLAN IN THE N_2O_4–DMF SYSTEM*

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ABSTRACT

By means of ^{13}C-n.m.r. spectroscopy the substituent distribution within the anhydroglucose and anhydroxylose units, respectively, in the systems N_2O_4–DMF–cellulose, N_2O_4–DMF–xylan, N_2O_4–DMF–SO_2–cellulose, N_2O_4–DMF–SO_2–xylan, N_2O_4–DMF–SO_3–cellulose, and N_2O_4–DMF–SO_3–xylan has been investigated. In the systems containing cellulose, a derivatization exclusively at C-6 is observed on dissolution in N_2O_4–DMF and on subsequent reaction with SO_2, while with SO_3 as the acylating agent some substitution also takes place on the secondary OH groups at higher d.s. The OH groups of xylan are substituted to a rather low d.s. by nitrite ester groups in the system N_2O_4–DMF and by sulphate half-ester groups on subsequent reaction with SO_2 or SO_3. The results are discussed on the basis of a transesterification from the nitrite to the sulphate ester.

INTRODUCTION

Most early work on the conversion of cellulose into esters of strong acids was performed in heterogeneous reaction systems, which often gave products having poor solubility and/or low d.p. due to serious degradation. Cellulose nitrate formation may be considered an exception rather than a rule. The problem of serious chain degradation was already noticed by Freudenberg[1] in his early work on the interaction between cellulose and inorganic acids, and obviously it was principally responsible for the very limited attention that cellulose sulphate half-esters received in the following decades. However, the successful search for new, nonaqueous cellulose solvents, dating from the end of the sixties, stimulated investigations on the acylation of cellulose in various nonaqueous media under homogeneous reaction conditions. These experiments resulted in the synthesis of new cellulose esters,

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*Dedicated to the memory of Karl Freudenberg on the centenary of his birth.

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as well as in new routes to conventional cellulose esters having complete solubility at low degrees of substitution.

Starting from unsubstituted cellulose and the variety of nonaqueous solvent systems known today, two general routes to cellulose esters are feasible[2]: (*a*) dissolution of the polymer in a "nonderivatizing" solvent system acting *via* H-bonded complex formation, and subsequent homogeneous reaction with a suitable acylating agent, or (*b*) dissolution in a "derivatizing" solvent system acting *via* formation and solvation of an unstable cellulose derivative, and subsequent introduction of the desired acyl groups coupled with elimination of the primary, unstable substituents.

For the preparation of cellulose sulphate, the latter way proved to be successful. As shown by Schweiger[3,4] and by us[5,6], cellulose sulphates having medium and low d.s. and giving highly viscous solutions in water can be obtained by dissolving cellulose in dinitrogen tetroxide-*N,N*-dimethylformamide (N_2O_4–DMF), which primarily leads to the formation of unstable cellulose nitrites[7,8], and subsequent reaction with sulphur trioxide[3,4,9] or with sulphur dioxide[5,6]. In the latter case we consider $NOSO_4H$ to be the active sulphating agent[6].

As with other partially substituted cellulose derivatives, the distribution of substituents within the anhydroglucose units (AGU) of cellulose sulphates is a question of scientific relevance and potential importance with regard to the properties that are required for particular end-uses[10,11]. In recent publications, somewhat contradictory conclusions were drawn with regard to preference for the primary or one of the secondary hydroxyl groups in cellulose sulphation[9,12]. We therefore started a systematic study by ^{13}C-n.m.r. spectroscopy of the distribution of sulphate half-ester groups in relation to some parameters of the acylation process, especially the sulphating agent and the water content of the system at the end of the reaction.

Also the constitution of the DMF–N_2O_4–cellulose system prior to sulphation was included in the investigation, and some experiments were performed with a beechwood xylan as a model substrate devoid of primary OH groups. The results are summarized and discussed in the present paper.

EXPERIMENTAL

Materials. — A hydrolytically degraded and subsequently disintegrated cellulose powder from spruce sulphite pulp (Heweten 10 HZ®, VEB Papierfabrik Weißenborn, G.D.R.) with d.p.$_{Cu}$ ~160 was used for most of our experiments. For comparison, a sample of beechwood xylan prepared by alkali extraction of milled beechwood was employed. Data on the composition of this sample before and after water extraction are summarized in Table I. A comparison between the original and the water-extracted samples reveals no significant difference in d.p. and in the content of anhydroxylose units.

The N_2O_4 was supplied at a purity of ≥95% by the chemical industry. The SO_2 was a commercial technical-grade product, and SO_3 was obtained by distillation from fuming sulphuric acid. The DMF used as the reaction medium was first

TABLE I

ANALYTICAL DATA FOR BEECHWOOD XYLAN SAMPLES

Property measured	*Sample*	
	Original	*Water-extracted*
D.p. (cuprammonium solution)	138	139
Pentosan content (Jayme-Sarten)	81%	85%
Solubility in H_2O	36%	—
Solubility in 6% aqueous NaOH	100%	100%

distilled and then treated with a suitable molecular sieve (Zeosorb 5IM) to bring the residual content of H_2O to less than 0.01%.

Synthesis and after-treatment of the cellulose and xylan sulphates. — Samples of 40 g of oven-dried (105°) cellulose powder were swollen overnight in 100 mL dry DMF and stirred at ~20° in a mixture of 150 mL DMF and 68 g N_2O_4 (3 mol N_2O_4 per mol AGU), to give clear brownish-green solutions within 1 h. Sulphation was performed in these solutions by reaction either with SO_2 (2 mol per mol AGU, dissolved in DMF) for 3 h at 30°, or with SO_3 (1 mol per mol AGU, 10% solution in DMF) for 3 h at 10°. The clear, homogeneous reaction mixtures were kept overnight at room temperature, then subdivided into two parts, and one part was processed in each of the following ways: (*a*) precipitation and washing of the H^+ cellulose sulphate with 1:3 v/v EtOH–acetone, and neutralization with 2% NaOH in EtOH under heterogeneous conditions; and (*b*) addition of 5 parts of H_2O per part cellulose to the reaction mixture for 15 min, then precipitation of the H^+ cellulose sulphate by adding acetone, washing with EtOH–acetone, and neutralization with NaOH in EtOH as stated in *a*.

After drying and swelling in DMF as stated for cellulose, the original xylan could not be completely dissolved in the N_2O–DMF system even after the addition of 6 mol N_2O_4 per mol anhydroxylose unit (AXU) and keeping overnight. But by treatment of this mixture with 2 mol SO_2 per mol AXU for 4 h at 30° and keeping overnight at room temperature, most of the polymer was dissolved. The decanted liquid phase was divided into two parts and one part each processed as follows: (*a*) precipitation with EtOH, washing with 1:3 v/v EtOH–acetone, then neutralization with 2% NaOH in EtOH; and (*b*) addition of 5 parts of water per part xylan for 15 min, precipitation with acetone, washing and neutralization as in *a*.

The water-extracted xylan was solvent-exchanged with dry DMF and it could then easily be dissolved in N_2O_4–DMF with 4 mol N_2O_4 per mol AXU. Sulphation was performed with 1 mol SO_3 per mol AXU overnight at room temperature. The mixture was divided into two parts and one part each processed as just described.

The d.s. of all cellulose and xylan sulphate samples was calculated from the sulphur content, which was determined according to ref. 4.

N.m.r.-spectroscopic investigations. — The ^{13}C-n.m.r. spectroscopic meas-

TABLE II

EFFECT OF THE CONDITIONS OF SYNTHESIS ON THE D.S. AND VISCOSITY OF CELLULOSE AND XYLAN SULPHATE SAMPLES

Sample no.	*Starting material*	*Sulphating agent (amount)*[a]	*Addition of water*	*After-treatment*	*D.s.*	$\eta_{1\%}^{20°}$ *(mPa.s)*
CS*1*	Cellulose	SO_2(2)	–	Acetone, EtOH, NaOH in EtOH	0.69	2.8
CS*2*	Cellulose	SO_2(2)	+	Acetone, EtOH, NaOH in EtOH	0.66	3.5
CS*3*	Cellulose	SO_3(1)	–	Acetone, EtOH, NaOH in EtOH	0.56	4.0
CS*4*	Cellulose	SO_3(1)	+	Acetone, EtOH, NaOH in EtOH	0.86	2.2
CS*5*	Cellulose	SO_3(2)	–	Acetone, NaOH in EtOH	1.06	1.5
CS*6*	Cellulose	SO_3(1.5)	+	Acetone, NaOH in EtOH	1.30	3.7
XS*1*	Xylan	SO_2(2)	–	Acetone, EtOH, NaOH in EtOH	0.17	1.9
XS*2*	Xylan	SO_2(2)	+	Acetone, EtOH, NaOH in EtOH	0.20	1.7
XS*3*	Xylan	SO_3(1)	–	Acetone, EtOH, NaOH in EtOH	0.51	2.5
XS*4*	Xylan	SO_3(1)	+	Acetone, EtOH, NaOH in EtOH	0.55	2.8

[a] Moles per mole of anhydropyranose unit.

urements were performed with a Bruker WP 200 instrument operating at a spectrometer frequency of 50.327 MHz in the pulsed Fourier-transform mode with proton decoupling. From 3000 to 5000 scans were taken on each sample. Tetramethylsilane was employed as an internal standard.

The spectrum of the original xylan was obtained after dissolving it in a solution of 6% NaOH in D_2O. Spectra of the N_2O_4–DMF–cellulose and N_2O_4–DMF–xylan solutions were recorded after the addition of a small amount of dimethyl sulfoxide-d_6. The cellulose and xylan sulphates were dissolved in D_2O to a polymer concentration between 5 and 10%, depending on sample viscosity.

RESULTS

Analytical data for cellulose and xylan sulphates. — All the Na cellulose sulphate and Na xylan sulphate samples discussed here were completely soluble in water. The d.s.-values and viscosities (1% aqueous solutions, 20 ±0.1°, Ubbelohde viscosimeter) of our samples are summarized in Table II, together with some remarks on synthesis and after-treatment.

The d.s.-values of the cellulose sulphate samples are within the range 0.5 to 1.3, while the d.s. of the xylan sulphates is definitely lower. A significant increase in d.s. due to the addition of water at the end of the reaction is observed with cellulose on sulphation with SO_3, but not with SO_2. In the case of xylan no significant change in d.s. was observed on addition of water with either SO_2 or SO_3 as the sulphating agent.

The solution viscosity is rather low for all the samples, due to the low d.p. of the starting materials.

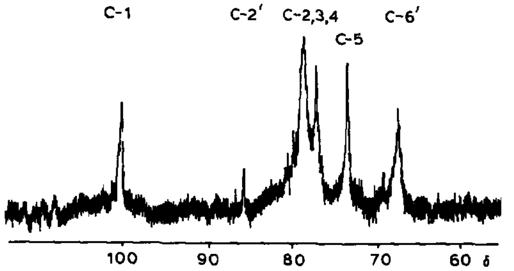

Fig. 1. ^{13}C-N.m.r. spectrum of cellulose dissolved in N_2O_4–DMF.

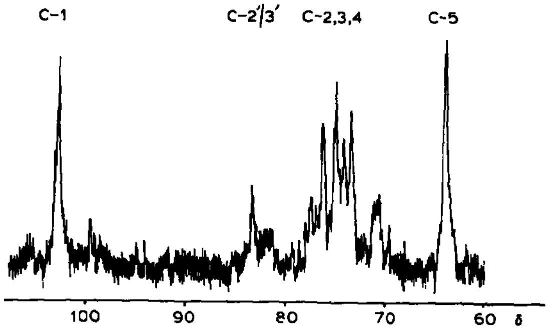

Fig. 2. ^{13}C-N.m.r. spectrum of xylan dissolved in N_2O_4–DMF.

^{13}C-N.m.r. spectroscopic investigation. — The spectra of cellulose and xylan after dissolution in the N_2O_4–DMF system are shown in Figs. 1 and 2. A comparison with the signals of the original polymers dissolved without derivatization is included in Table III. The C-6 signal of cellulose is shifted about 7 p.p.m. to lower field in N_2O_4–DMF and the corresponding signal of unsubstituted cellulose is no longer detectable, indicating complete substitution at C-6. In the C-2–C-3 region, on the other hand, the signals of the unsubstituted cellulose are predominant, and only a very small additional signal is visible at lower field. In the case of xylan, however, a rather high degree of substitution at the secondary OH groups is indicated by the position and intensity of the signals. With cellulose as well as with xylan the signal of C-1 remains unaffected by the interaction with N_2O_4.

The spectral data for our sulphated samples are presented in Table III, where the signal positions are compared to those of the nonderivatized polymers. As already stated in our previous communication[13], the sulphation of cellulose dissolved in N_2O_4–DMF, with SO_2 as well as with $NOSO_4H$, occurs exclusively at the C-6 position. This is confirmed for a d.s. of about 0.7 by the data for sample CS*1*, which is representative of the SO_2-sulphated samples prepared without addition of water at the end of the reaction. The addition of water (CS*2*) did not lead to changes in the height and position of the ^{13}C-n.m.r. signals.

This situation is changed, however, if SO_3 is employed as the sulphating

TABLE III

^{13}C-N.M.R. CHEMICAL SHIFTS OF CELLULOSE SULPHATE (CS) AND XYLAN SULPHATE (XS)

Sample (sulphating agent)	*Chemical shifts (δ)*							
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-2'–C-3'*[a]	*C-6'*[a]
CS*1* (SO_2)	102.9 100.9	74.4	75.2	78.7	73.4	60.4		66.8
CS*2* (SO_2 + H_2O)	102.9 100.9	74.5	75.3	78.8	73.4	60.4		67.0
CS*3* (SO_3)	102.8	74.5	75.3	78.9	73.4	60.5		66.9
CS*4* (SO_3 + H_2O)	102.7	74.4	75.3	78.9	73.4	60.5		66.8
CS*5* (SO_3)	102.8 100.8	74.3	75.2	78.8	73.3	60.5	80.1	66.2
CS*6* (SO_3 + H_2O)	102.8	74.4	75.5	78.4	73.4	60.5	80.2	66.4
Cellulose[b]	102.5	73.1	75.3	79.3	74.7	60.5		
Cell–N_2O_4–DMF	99.6	76.8	78.6	78.2	73.0		85.2	66.9
XS*1* (SO_2)	102.1	73.1	74.1	76.8	63.3		82.8/79.5	
XS*2* (SO_2 + H_2O)	102.1	73.1	74.0	76.7	63.4		82.7	
XS*3* (SO_3)	102.2/100.5	73.2	74.1	76.8	63.3		82.7/79.6	
XS*4* (SO_3 + H_2O)	102.3/100.3	73.2	74.1	77.2	63.5		82.7/79.5	
Xylan	102.7	73.7	75.4	76.3	63.7			
Xylan–N_2O_4–DMF	102.7	73.3	74.9	76.2	63.9		83.3	

[a] Primed numbers refer to substituted (acylated) positions. [b] Ref. 14.

agent, as demonstrated by the data for samples CS*3*–CS*6*. With these low-d.s. cellulose sulphates exclusive C-6 substitution is indicated by the data, but the height of the substituted C-6 signal increased significantly in sample CS*4*, prepared by addition of water at the end of the sulphation reaction. The increase corresponds to the difference in total d.s. between these two samples.

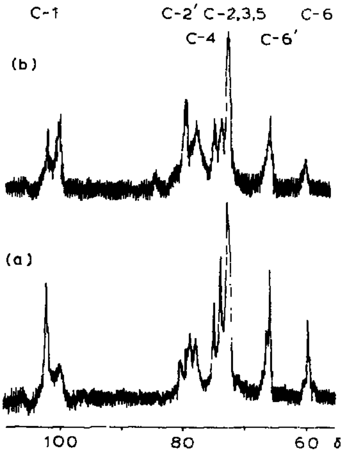

Fig. 3. ^{13}C-N.m.r. spectra of medium-d.s. Na cellulose sulphates prepared by sulphation with SO_x. Key: (a) without addition of water (CS*5*); (b) with addition of water (CS*6*).

On the other hand, two samples also sulphated with SO$_3$, but to a higher d.s., not only show a remarkable enhancement in total d.s. from 1.06 to 1.30 when water is added at the end of the reaction, but also a significant change in sulphate-group distribution (Fig. 3). In the absence of water, C-6 substitution is predominant in these samples, but the secondary OH groups have reacted to some extent. With the addition of water, however, the increase in total d.s. is accompanied by an increase in the ratio of C-2–C-3 to C-6 substitution. The signal intensity of C-6 remains nearly the same in both the spectra, but that for substituted C-2 and C-3 is increased considerably.

Changes in the shape of the C-1 signal due to the addition of water after sulphation with SO$_3$ were noted. In the absence of water a splitting of this signal is only faintly indicated, but a division into two separate peaks of about equal height becomes clearly visible after addition of water. Obviously, this splitting of the C-1 signal correlates well with the extent of substitution at the C-2 atom indicated in the spectrum.

In the original xylan sample dissolved in aqueous NaOH, the amount of anhydrohexose units present was too small to give a detectable C-6 signal. Thus also in the ^{13}C-n.m.r. spectra of our Na xylan sulphates (Fig. 4) no C-6 signal (unsubstituted or substituted) could be found.

As to be expected from the values of d.s. <1.0, signals of substituted as well as unsubstituted C-atoms are found in the C-2–C-3 region, and additionally a splitting of the C-1 signal due to partial substitution of the secondary OH groups is observed. The n.m.r. spectra are to some extent dependent on the acylation agent employed and on the water content at the end of the sulphation reaction. After sulphation with SO$_2$ (samples XS*1* and XS2) about the same amount of substitution

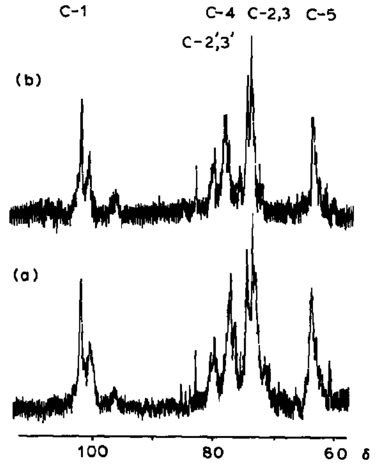

Fig. 4. ^{13}C-N.m.r. spectra of Na xylan sulphates prepared by sulphation with SO$_3$. Key: (a) without addition of water (XS*3*); (b) with addition of water (CS*4*).

at C-2 and C-3 can be inferred from the spectrum of the sample prepared without addition of H_2O, while after the addition of water only a single signal was found. With SO_3 as the sulphating agent, two signals are visible in the C-2–C-3 region of the spectrum (Fig. 4), with no detectable changes induced by addition of water.

DISCUSSION AND CONCLUSIONS

In the present work cellulose and a xylan of about the same d.p. were compared with regard to interaction with the systems N_2O_4–DMF, N_2O_4–DMF–SO_2, and N_2O_4–DMF–SO_3. The purpose was to obtain more comprehensive information on the reactivity of the primary and secondary OH groups of cellulose during dissolution and subsequent homogeneous sulphation in these systems. Dissolution of isolated and dried xylan in the N_2O_4–DMF system proceeded rather slowly and incompletely as compared to native cellulose under similar conditions of pretreatment. An analogous difference between cellulose and xylan has been observed on dissolving these polymers in the *O*-basic, nonderivatizing solvent *N*-methylmorpholine *N*-oxide, and in several *O*-basic model systems neither xylan nor xylose could be dissolved, in contrast to glucose, cellobiose, and cellulose[15]. These observations support the idea of a rather strong interaction of the active species, or site of reaction of the solvent molecules, of these nonaqueous systems with the OH group at C-6. Such an interaction might be connected with the rather high acidity of this hydroxyl group[16]. On the other hand, xylan could be dissolved without difficulty in the N_2O_4–DMF system after solvent exchange in the swollen state.

From the ^{13}C-n.m.r. spectra of the systems N_2O_4–DMF–polysaccharide it can be concluded, in connection with our earlier synthetic and analytical work on nitrosyl compound–DMF–cellulose systems[8], that:

(*a*) A preferential chemical interaction of N_2O_4, with formation of the nitrite ester, occurs at the C-6 atom of cellulose, where substitution is obviously complete and the chemical shift of the ^{13}C-n.m.r. signal due to this substitution is comparable to that reported for cellulose nitrate formation[17].

(*b*) Even with a large excess of N_2O_4 the C-2–C-3 signals (and also that of C-1) remain largely unaffected in the case of cellulose, while with xylan a partial substitution at the secondary OH groups is indicated by additional signals.

(*c*) N_2O_4 in DMF obviously interacts with the OH groups of polysaccharides *via* covalent substitution (formation of nitrite esters), giving rise to additional ^{13}C-n.m.r. signals, as well as *via* formation of an addition compound not affecting the ^{13}C-n.m.r. spectrum. Some kind of equilibrium may exist between covalent derivatization and addition compound formation, the position of this equilibrium depending on the reactivity of the different OH groups and on the conditions of reaction (*cf.* refs. 7–9, 13, and 18).

On reaction with SO_2 after previous dissolution of the polymer in the N_2O_4–DMF system, an exclusive sulphation at the C-6 position up to a d.s. of about 0.7 is observed with cellulose. D.s. values >0.9 have not been realized in this system.

With xylan a partial derivatization of the secondary OH groups to a rather low d.s. is accomplished, due to the absence of the more reactive primary OH group. Total d.s. and substituent distributions are not significantly affected by the addition of water to the system at the end of the sulphation reaction. As already mentioned, we assume that in this system the active sulphating agent is nitrosyl hydrogensulphate, $NOSO_4H$, which can be formed by a redox process between SO_2 and N_2O_4 *via* HNO_3 as an intermediate. The observation that $NOSO_4H$ added to a solution of cellulose in N_2O_4–DMF also sulphates the cellulose exclusively in the 6-position supports this assumption. We further conclude from our experimental results, obtained with cellulose and with xylan, that the homogeneous sulphation of these polymers with SO_2 or $NOSO_4H$ occurs *via* a transesterification of nitrite and sulphate ester groups according to the following equations:

$$\text{Cell-OH or Xyl-OH} + N_2O_4 \rightleftarrows \text{Cell-ONO or Xyl-ONO} + HNO_3$$
$$\text{Cell-ONO or Xyl-ONO} + NOSO_4H \rightleftarrows \text{Cell-OSO}_3\text{H or Xyl-OSO}_3\text{H} + N_2O_3.$$

The OH groups not previously transformed to nitrite ester groups obviously do not participate in this type of sulphation reaction. Possibly, a "protection" of these OH groups by prior formation of an addition compound with N_2O_4 may play some role. The lack of effect of the addition of water subsequent to the sulphation on d.s. and substituent distribution might be understood as a termination of this route to sulphate ester formation by inactivation of the active species, $NOSO_4H$.

With SO_3 as the acylating agent in the homogeneous sulphation of cellulose and xylan dissolved in N_2O_4–DMF, the results so far obtained are somewhat contradictory with regard to the influence of water added at the end of the reaction. In the absence of water, a C-6 substitution takes place exclusively at low d.s. and preferentially at medium d.s. in the case of cellulose, while with xylan, sulphation at the secondary OH groups is realized. Addition of water leads to an increase in the d.s. of cellulose sulphates but not of xylan sulphates. This increase in the d.s. of cellulose sulphate is definitely due to an additional derivatization at the secondary OH groups if the SO_3:AGU ratio employed is high enough to lead to d.s. >1. On the other hand, no evidence of C-2–C-3 substitution could be obtained from our spectra at an SO_3:AGU ratio of 1, which provides a total d.s. <1 (samples CS*3* and CS*4*). These results differ from those of Schweiger[9], who on the basis of a periodate oxidation of his samples concluded that sulphation takes place at secondary OH groups in the N_2O_4–DMF–SO_3–cellulose system even at the low d.s. of $\leqslant 0.45$.

In addition to the transesterification mechanism which is probably involved when SO_3 is the sulphating agent, a direct esterification of free OH groups should also be considered in this case. We suppose that this latter route can be favored by the presence of water, which decomposes the cellulose–N_2O_4 adduct and renders additional OH groups accessible for acylation, which will occur if an excess of acylation agent is still available. In contrast to the obviously fast decomposition of the N_2O_4–cellulose adduct, deactivation of the SO_3–DMF complex proceeds rather slowly in the presence of water. In this way, the relationship between the SO_3:AGU ratio, or the d.s., and the effect of water might be explained.

Finally, comparing cellulose and xylan with respect to interaction with the acylating systems considered here, it can be concluded that under the same conditions of reaction cellulose is derivatized to a much higher d.s. that xylan. This is due in part to the larger number of OH groups per monomer unit, but is mainly caused by the high reactivity of the primary OH group at C-6 in the formation of nitrite ester as well as in subsequent conversion into sulphate ester. This holds especially true for sulphation with SO_2, where secondary OH groups obviously react only if no primary ones are available. As far as can be concluded from our ^{13}C-n.m.r. spectra, no significant difference seems to exist between the two OH groups of xylan with regard to their reactivity in sulphate ester formation.

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