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# Novel cellulosic ethers with low degrees of substitution — I. Preparation and analysis of long-chain alkyl ethers

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Twenty 'hydrophobic' ethers (S1–S20) of hardwood cellulose were prepared by reaction with suitable alkane derivatives in the presence of alkali (sodium hydroxide or hydride) and either *iso*propanol or dimethyl sulfoxide. The alkylating reagents were the 1-bromo-, 1-iodo-, or 1,2-epoxy-derivatives of butane, octane, decane, dodecane, tetradecane, hexadecane and octadecane. The products were characterised by elemental analysis, FT-IR spectroscopy, thin layer chromatography (TLC) and [$^1$H](NMR) nuclear magnetic resonance degraded of samples by acetolysis and gas–liquid chromatography (GLC) and mass spectrometry (MS) of the alditol acetates prepared from the acetolysates. The capacities of the products to bind a hydrophilic dye (methylene blue) were also measured. Degrees of substitution (DS) ranging from <0·01 to 0·58 were found. All of the derivatives retained some of the fibrous character of the cellulose, and those of higher DS floated on water like cork.

## INTRODUCTION

Novel cellulose derivatives can exhibit surprising properties which provide abundant scope for scientific curiosity as well as possibilities for industrial applications. For many applications it is undesirable to disrupt or shorten the cellulose fibres, and hence there is a special interest in mild conditions for derivatisation, which result in only low degrees of substitution (DS). Long-chain alkyl substituents can bring about marked changes in the physical properties of cellulose, even at low DS, and ethers are of special interest because of their high stability in alkali and good stability in acid.

In recent years there has been emphasis on the development of milder and simpler methods for preparing cellulose ethers (Kondo & Gray, 1992), the control of substituent distribution in these products (Kondo & Gray, 1991), novel reagents and reaction conditions (Isogai *et al.*, 1984; Samaranayake & Glasser, 1993), and new analytical methods (Fyfe *et al.*,1983; Isogai *et al.*, 1986, 1993).

This paper reports the preparation and analysis of 20 derivatives obtained by reacting cellulose with alkyl halides and 1,2-epoxyalkanes at low temperatures and in the presence of swelling agents. These products are referred to informally as 'hydrophobic' ethers of cellulose, essentially because those of higher DS ( > 0·2) had the property of floating on water like cork.

## EXPERIMENTAL

### Materials

Cellulose flock was kindly supplied by Dr P. Mariotti, Chimica del Friuli S.p.A., Torviscosa (Italy). It was prepared from hardwood by the acidic calcium sulfite method, and bleached with chlorine and chlorine dioxide. Analytical data are given in Table 1. Portions (100 g) were further purified by washing twice with aqueous (0·8 w/v) diethylenetriaminopenta-acetic acid (DTPA; 5 l) (Merck, Darmstadt, Germany) adjusted to pH 7·0 with sodium hydroxide. The cellulose was then washed exhaustively with distilled water, followed by ethanol (95% w/w) (Vinmonopolet, Oslo, Norway), and air-dried. The product contained ash (450 ppm) and water (11% w/w).

1,2-Epoxybutane, 1,2-epoxyoctane, 1,2-epoxydecane,

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**Table 1. Characteristics of cellulose**

| | |
|---|---|
| CaO | 110 ppm |
| α-cellulose | 95·7% |
| Extracted by $CH_2Cl_2$ | 0·08% |
| Ash at 80°C | 1000 ppm |
| Pentosans | 1·9% |
| Copper number[a] | 0·5 g |
| Viscosity | 52 cP[b] |

[a] Determined by the Hägglund method (1930).
[b] Measured by the standard SNIA method (Mariotti, personal communication).

1-iodobutane, 1-bromooctane, 1-bromododecane, 1-bromotetradecane, 1-bromohexadecane, and 1-bromooctadecane were purchased from the Sigma Chemical Company (St. Louis, MO, USA) and 1,2-epoxyoctadecane from Aldrich (Steinheim am Albuch, Germany). The other reagents were purchased from Carlo Erba (Milan, Italy; RP chemicals), Fluka Chemie AG (Buchs, Switzerland) or Merck. All other chemicals were used as received.

## Derivatisation

The alkylating reagents were 1,2-epoxyalkanes or alkyl halides, as detailed above. Because of their insolubility in water, the reactions were carried out on cellulose suspended in *iso*propanol or dimethyl sulfoxide (DMSO), and activated by a strong base (sodium hydroxide or sodium hydride). Sodium hydride reacts with DMSO to give the anion $(H_3C\text{-}SO\text{-}CH_2)^-$, but it is not certain that this is the active base in the derivatisation (Corey & Chaykovsky, 1962; Hakomori, 1964; Ciucanu & Kerek, 1984). The cellulose was oven-dried (100°C, 6 h) before use. Five different procedures were followed. Twenty derivatives were obtained, which are named and labelled in Table 2.

### *Method A*

This was essentially the method of Klug (1963). To a vigorously stirred suspension of cellulose in *iso*propanol, aqueous (15·9% w/w) sodium hydroxide was added portionwise over a period of up to 1 h. The reagent was then added, and stirring was continued for 1–3 days. The reaction was then quenched by addition of distilled water (1 l). The derivatised cellulose was collected by vacuum filtration, first washed with water acidified with acetic acid, followed by pure water, ethanol, and finally air-dried.

### *Method B1*

Cellulose was mixed by grinding in a mortar and pestle with a mixture of DMSO and the reagent. The mixture was maintained for 1–3 h at 22°C to permit maximal swelling and penetration of the reagent into the fibres. Finely ground sodium hydroxide (1·1 mol) was then added as a suspension in DMSO, with vigorous grinding. The mixture was then retained at 22°C for 24–32 h with periodic grinding. The fibres were then collected on a sintered glass filter, and washed successively with DMSO, water, dilute acetic acid, a large quantity of water and finally ethanol. The product was air-dried.

**Table 2. Experimental conditions for the derivatisation reactions**

| Derivative | Weight of cell (g) | Method | Reactant | Amount (mol) | Base | Suspending agent | Reaction time (h) |
|---|---|---|---|---|---|---|---|
| S1 | 20 | A | 1,2-epoxybutane | 0·14 | NaOH | *iso*propanol | 30 |
| S2 | 20 | A | 1,2-epoxybutane | 0·28 | " | " | 45 |
| S3 | 20 | A | 1,2-epoxybutane | 0·56 | " | " | 45 |
| S4 | 10 | A | 1,2-epoxyoctane | 0·08 | " | " | 42 |
| S5 | 10 | A | 1,2-epoxyoctane | 0·31 | " | " | 67 |
| S6 | 10 | B1 | 1,2-epoxydecane | 0·13 | " | DMSO | 24 |
| S7 | 10 | B2 | 1-iodobutane | 0·20 | " | " | 50 |
| S8 | 10 | B1 | 1,2-epoxyoctadecane | 0·03 | " | " | 32 |
| S9 | 10 | B1 | 1,2-epoxyoctadecane | 0·06 | " | " | 32 |
| S10 | 10 | B2 | 1-bromooctadecane | 0·10 | " | " | 92 |
| S11 | 10 | B2 | 1-bromohexadecane | 0·10 | " | " | 48 |
| S12 | 10 | B2 | 1-bromotetradecane | 0·10 | " | " | 133 |
| S13 | 10 | C1 | 1-bromooctadecane | 0·10 | NaH | " | 72 |
| S14 | 10 | C1 | 1-bromododecane | 0·10 | " | " | 15 |
| S15 | 10 | C1 | 1-bromotetradecane | 0·10 | " | " | 25[a] |
| S16 | 8·5 | C1 | 1-bromohexadecane | 0·08 | " | " | 19 |
| S17 | 5 | C1 | 1-bromooctane | 0·05 | " | " | 3 |
| S18 | 5 | C2 | 1-bromooctane | 0·05 | " | " | 25 |
| S19 | 5 | C2 | 1-bromooctadecane | 0·05 | " | " | 26 |
| S20 | 5 | C2 | 1-bromotetradecane | 0·05 | " | " | 26 |

[a] The suspension of NaH in DMSO was heated to 40°C to accelerate the formation of the anion $(CH_3\text{-}SO\text{-}CH_2)^-$. The cellulose was added after cooling to room temperature.

*Method B2*
This procedure resembled B1, except that the cellulose was first fully swollen by grinding with the DMSO and sodium hydroxide, after which the reagent was added with thorough mixing.

*Method C1*
Sodium hydride was slowly added to DMSO with gentle mechanical stirring, and stirring at 22°C was continued overnight. Dry cellulose was added portionwise, and after it was fully swollen (3–9 h), the reagent was added and stirring at 22°C was continued for 3–72 h. The fibres were then collected, washed and dried as described for method B1.

*Method C2*
This procedure resembled C1, but the cellulose was first swollen in a mixture of DMSO and the reagent for 3–24 h. The previously prepared solution of sodium hydride in DMSO was then added to this mixture, and the reaction was allowed to proceed at 22°C for a further period of 24–26 h. In one case (S15), the suspension of sodium hydride in DMSO was heated for 1 h at 40°C to promote formation of the anion $(H_3C\text{-}SO\text{-}CH_2)^-$, and then cooled to 22°C before mixing with the swollen cellulose.

The derivatives labelled S11, S12, S19 and S20 were additionally washed with acetone before drying. No attempt was made to exclude atmospheric oxygen in any of the experiments. The yields of pure white or pale yellow, fibrous products were essentially quantitative throughout.

## Analysis

*Solubility in organic solvents*
Qualitative tests were carried out to evaluate the solubilities of the derivatives in tetrahydrofuran, *iso*propanol, pyridine, *m*-xylene, other isomers of xylene, methanol, *N*,*N*-dimethylacetamide, ethyl acetate, dichloromethane, chloroform, diethylether, DMSO, dioxane, *n*-butanol, benzene, acetone, *n*-pentane, *n*-hexane and *n*-heptane. Portions (10 mg) of each derivative were stirred overnight in capped vials with portions (5 ml) of each solvent at 22°C. After centrifugation, the appearance of the undissolved fibres was compared with that of the untreated fibres. The supernatants were evaporated to dryness on watch glasses and any residue was compared under the lens with any residue from the same volume of pure solvent. When a significant residue was found, a portion of the original supernatant was mixed with an excess of a miscible non-solvent (water or methanol). Any precipitate was collected (centrifuge), redissolved in the original solvent, and mixed again with an excess of non-solvent. Any precipitate was taken as evidence of solubility of the derivative in the original solvent.

*Accessibility to methylene blue*
In a quest for a simple, arbitrary criterion or measure of 'hydrophobicity', the capacities of the derivatives to occlude various hydrophobic and hydrophilic dyes was investigated. A suitable procedure was developed for the hydrophilic dye, methylene blue (3,9-bisdimethylaminophenazothionium chloride). It was assumed that this dye would, as in partition chromatography on paper, distribute itself between solid and solution in a proportion that would depend primarily upon the water-content of each. The reagent was a solution (0·14 mM) of methylene blue in aqueous ehtanol (17% v/v). Portions (10–100 mg) of cellulose derivative were shaken vigorously with portions (5 ml) of this reagent. After centrifugation, the supernatants were diluted appropriately with water–ethanol and their absorbances at 668 nm were measured in a Varian Cary 2200 spectrophotometer (Varian Techtron, Mulgrave, Victoria, Australia), employing 1 cm quartz cuvettes. Accessibility was expressed as the difference in absorbance between the untreated reagent solution and the supernatants.

*Acetolysis*
Portions (100 mg) of cellulose derivative were dispersed in portions (4 ml) of acetic anhydride – sulfuric acid (9:1 v/v, freshly mixed) at 22°C. These mixtures were shaken gently at 40°C until all the particles had dissolved (2–5 days). The solutions were then poured on to crushed ice (100 ml), and the gummy precipitates were washed with distilled water until the washings were neutral. The residues were dissolved in chloroform (50 ml), and the solutions were dried with anhydrous sodium sulfate, filtered, and evaporated to dryness.

*Products of acetolysis*
TLC was carried out essentially as described by Tate and Bishop (1962). Silica-gel plates (Merck Fertigplatten, Kieselgel 60) were irrigated with benzene–methanol (96:4, v/v). Sugar acetates were visualised by spraying with water (Tate & Bishop, 1962) or by charring with ammonium bisulfate reagent (Ziminsky & Borowski, 1966; Gal, 1968). Unsaturated sugar derivatives resulting from dehydration reactions were detected by examining the plates under u.v. light. The spots were further emphasised by exposing the plates to iodine vapour, or by spraying with sulfuric acid. [$^1$H]NMR spectroscopy of the crude acetolysates was performed on solutions in deuterochloroform in a JEOL FX-100 spectrometer (Akishima, Tokyo, Japan).

*Gas–liquid chromatography – mass spectrometry (GLC–MS) of alditol acetates*
The crude acetolysates were further degraded to monosaccharides and their derivatives by methanolysis, followed by hydrolysis, and then by conversion into alditol acetates as described by Albersheim *et al.* (1967).

GLC of these products was performed on a Hewlett-Packard 5890 GC (Avondale, Pennsylvania, USA), equipped with a HP-1 Ultra-1 or an SP-2340 capillary column, and a flame-ionisation detector. The injection capillary was employed in split-mode. A Hewlett-Packard HD5971 A mass spectrometer was coupled with the GLC apparatus.

*Elemental analysis*

This was performed on a Carlo Erba Model 1106 elemental Analyser, by Dr E. Cebulec in the Analytical Laboratory, Department of Chemical Sciences, University of Trieste. Samples were first dried *in vacuo* at 105°C over anhydrous calcium sulfate for 12 h. Their water content was then determined by the Karl-Fischer method, using a Mettler DL18 apparatus (Mettler Instruments AG, Greifensee, Switzerland), and the data from the elemental analyser were corrected accordingly.

*IR spectroscopy*

The measurements were performed in the Laboratory of POLY-biòs Research Centre, Area Science Park, Padriciano, Trieste, Italy. The instrument was a Perkin-Elmer Model 1750 single-beam spectrophotometer (Norwalk, CT, USA) coupled to a Perkin-Elmer 7300 computer, which processes the signals from 16 to 32 scans into their Fourier transform. The cellulose derivatives were dried over silica gel *in vacuo* overnight at 22°C. Portions (2 mg) were then mixed with portions (200 mg) of dry potassium bromide (Wilmad Glass, New York, USA). The mixtures were converted into pellets with a 10-ton press.

## RESULTS

### Solubilities

The DS were in general too low to impart solubility in organic solvents. Only in the case of S16 was a partial solubility in ethyl acetate detected. Chloroform and dichloromethane also removed traces of soluble material from a few derivatives. The flocks of fibres were, however, mostly disaggregated by the solvents, and significant swelling was evident in some cases.

### Accessibility to methylene blue

The results (Fig. 1) showed that the swelling effect of the strongly basic reaction conditions greatly increased the accessibility to methylene blue, but that in some cases, notably those in which higher DS values were subsequently found, the alkyl ether groups had decreased the nett accessibility to values below that of the original cellulose.

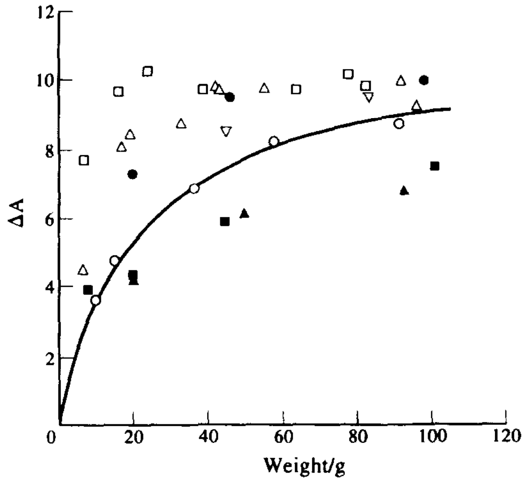

Fig. 1. Sorption of methylene blue at $\lambda = 668$ nm from 17% v/v aqueous ethanol by portions of: ○, untreated cellulose; □, cellulose swollen in NaOH/DMSO; ▽, cellulose swollen in NaOH/*iso*-propanol; △, cellulose swollen in NaH/DMSO; ●, S5; ■, S7; ▲, S17. ΔA is the difference in absorbance before and after shaking the methylene blue solution with cellulose (see text).

### TLC of acetolysates

Some typical $R_f$ values are shown in Table 3. As expected, unsubstituted cellulose gave a polymer-homologous series of the peracetates of α-D-glucopyranose, cellobiose, cellotriose, cellotetraose, etc. In addition, there were products of acid-catalysed dehydration reactions, which migrated as a single streak from the origin. The $R_f$ values were not accurately reproducible on separately developed plates, but the presence of the same sugar acetates and dehydration products was evident also in the acetolysates of the derivatised celluloses. All of these also contained a few other components, whose $R_f$ values slightly differed from those of the named peracetates. These components were, therefore, inferred to be the peracetates of alkyl ethers of the same sugars.

*[$^1$H]NMR of the acetolysates*

A typical spectrum is shown in Fig. 2. The signals at 1·2 and 0·8 ppm correspond to methylene and methyl protons, respectively, and ideally the ratio of their peak areas should precisely characterise the alkyl substituents. In practice there was poor agreement with the known identities of these substituents, and poor reproducibility with different samples and acetolysis conditions. This was evidently due to the presence of impurities in which the $CH_3/CH_2$ ratio was different from that of the intended alkyl substituent. It is natural to suspect ethanol as a likely impurity, since this solvent had been used to wash both the original cellulose and its etherified derivatives prior to acetolysis. Acetone was also used for washing in some cases. Whereas the adopted drying procedures are normally adequate to

**Table 3. TLC of acetolysates of alkyl ethers of cellulose**

| Cellulose derivative | $R_f$ values | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Cellulose | 0·09 | 0·13 | 0·18 | 0·28 | 0·48 | | | | | |
| Cellobiose octa-acetate | 0·28 | | | | | | | | | |
| S1 | 0·22 | 0·28 | 0·31 | 0·47 | | | | | | |
| S2 | 0·19 | 0·28 | 0·31 | 0·47 | 0·68 | | | | | |
| S3 | 0·21 | 0·29 | 0·32 | 0·47 | | | | | | |
| S4 | 0·03 | 0·05 | 0·07 | 0·11 | 0·13 | 0·17 | 0·21 | 0·24 | 0·29 | 0·41 |
| S5 | (tail) | 0·38 | | | | | | | | |
| S6 | 0·02 | 0·04 | 0·05 | 0·07 | 0·09 | 0·11 | 0·13 | 0·21 | 0·25 | 0·42 |
| S7 | 0·51 | 0·56 | 0·60 | 0·62 | | | | | | |
| S8 | 0·09 | 0·14 | 0·18 | 0·22 | 0·25 | 0·28 | 0·30 | 0·42 | | |
| S9 | 0·12 | 0·18 | 0·28 | 0·33 | 0·58 | | | | | |
| S10 | | 0·07 | 0·11 | 0·14 | 0·27 | 0·62 | | | | |
| S12 | 0·12 | 0·14 | 0·18 | 0·26 | 0·33 | 0·53 | 0·56 | 0·61 | | |
| S14 | 0·11 | 0·15 | 0·23 | 0·28 | 0·34 | (other?) | | | | |
| S15 | 0·10 | 0·15 | 0·22 | (0·24) | 0·32 | (0·38) | | | | |
| S17 | 0·09 | 0·15 | 0·23 | 0·29 | 0·48 | | | | | |
| S18 | (tail) | 0·45 | 0·54 | 0·60 | | | | | | |
| S19 | 0·07 | 0·14 | 0·23 | 0·29 | | | | | | |
| S20 | 0·06 | 0·14 | 0·23 | | | | | | | |

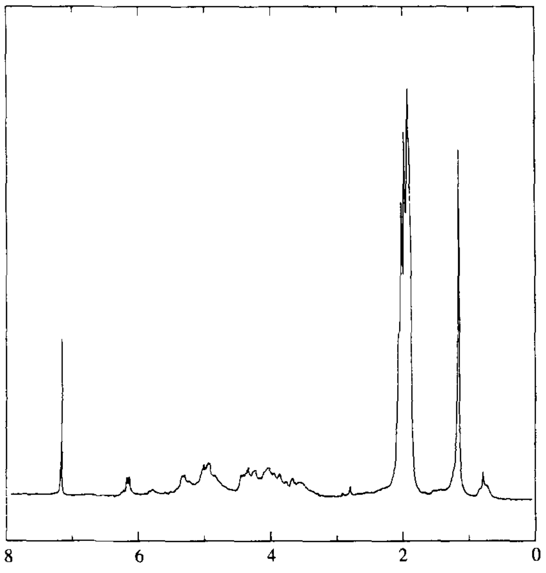

**Fig. 2.** [$^1$H]NMR spectrum of the acetolysate of S16 in $CDCl_3$ at 100 MHz.

remove such solvents from polysaccharides in general, etherified cellulose may have an exceptional affinity for them. The presence of this impurity gave, as expected, spuriously low values for the chain lengths of the alkyl ether groups.

## GLC–MS of alditol acetates

The crude acetolysates were converted into the acetates of alditols and their alkyl ethers by sequential methanolysis, hydrolysis, borohydride reduction and acetylation. Figure 3 shows a typical gas chromatogram of the products, and one with some standard alditol acetates. The main peak with a retention time of 21·3 min is clearly derived from D-glucose, while those at 15·6 and 16·0 min originate from dehydration reactions occurring during acetolysis. In addition, there is a minor component at 22·7 min, and a major one at 25·2 min. The e.i.–m.s. spectrum of the latter is shown in Fig. 4. The numerous fragments differing in $m/z$ by the mass of a methylene group (14 Da) provide the strongest evidence that long-chain alkyl groups are covalently linked to cellulose in the derivatives.

## Elemental analysis

The results are collected in Table 4, together with the calculated values of the degrees of substitution ($DS_{EA}$). The samples were not dried completely prior to analysis, as the severe conditions required for this could cause chemical degradation (pyrolysis). The samples were, therefore, dried under relatively mild conditions; the residual water (4–8%) was then determined in a separate experiment, and the results were used to correct the weights of the samples for elemental analysis. This water of hydration did not interfere with the analysis of organic hydrogen, because it evaporated immediately after the samples were introduced into the combustion oven, at a temperature of 300°C. For samples S7, S10 and S14 and the parent cellulose this was also confirmed by analysing directly for organic oxygen as well as for carbon and hydrogen.

## Infrared spectroscopy

The peak areas, $A_{OH}$ and $A_{CH}$, corresponding to O-H stretching (3700–3000 cm$^{-1}$) and C-H stretching (3000–2750 cm$^{-1}$) respectively, were computed with a digital integrator, and tentatively assumed to be proportional

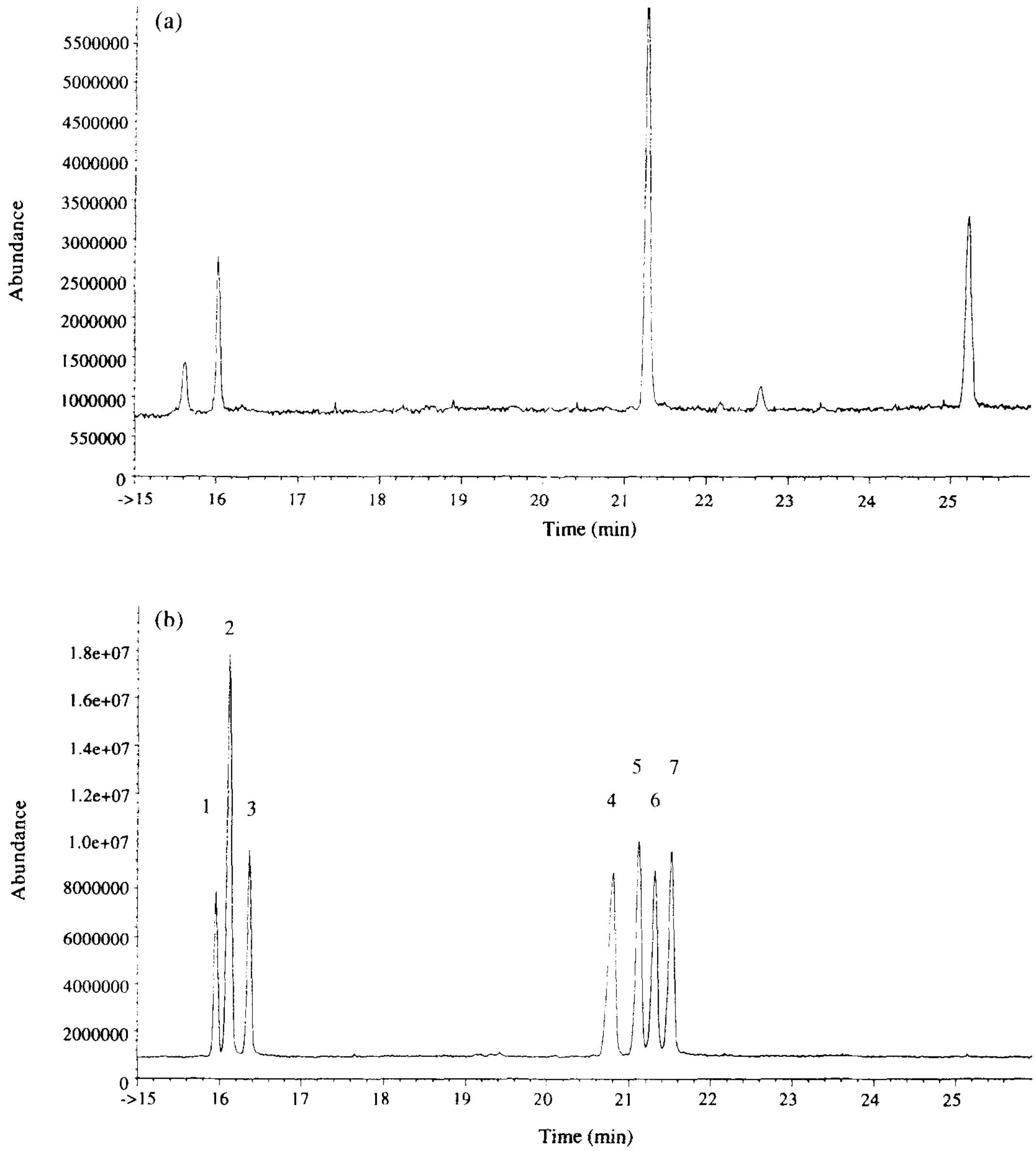

**Fig. 3.** (a) GLC of alditol acetates from acetolysate of S10. (b) GLC of alditol acetates of: 1, ribose; 2, arabinose and fucose; 3, xylose; 4, *myo*-inositol; 5, mannose; 6, glucose; 7, galactose.

to the amounts of these linkages, regardless of whether they were present in glucopyranose rings or alkyl substituents. For unsubstituted cellulose, the experimental value of the ratio, $A_{OH}/A_{CH}$, was found to be 11·0. Since this corresponded to a numerical ratio, $N_{OH}/N_{CH}$, of 3/7, it was possible tentatively to write:

$$N_{OH}/N_{CH} = [A_{OH}/A_{CH}]\cdot(3/7)/11. \qquad (1)$$

For the derivatised celluloses, the average value of $N_{OH}/N_{CH}$ for the individual β-D-glucopyranosyl units could be expressed as a function of the degree of substitution:

$$N_{OH}/N_{CH} = \frac{[\mathrm{DS}\cdot m + (1-\mathrm{DS})\cdot 3]}{[\mathrm{DS}\cdot n + (1-\mathrm{DS})\cdot 7]}, \qquad (2)$$

where $m$ and $n$ are, respectively, the numbers of O-H and C-H groups present in the monosubstituted glucosyl units (DS = 1).

The experimental values of $A_{OH}/A_{CH}$ for the derivatives are shown in Table 4 and illustrate the sensitivity of the method to both DS and the identities of the alkyl substituents. Table 4 also gives the values of $\mathrm{DS_{IR}}$ calculated from equations (1) and (2). Since the extinction coefficients of the C-H groups are unlikely to be the same in the alkyl side-chains as in the glucose rings, values ($\mathrm{DS_{IR}}^*$) were also calculated upon the assumption that they were 50% higher in the former. The results (Table 4) show much better agreement with the values of $\mathrm{DS_{EA}}$ determined independently by elemental analysis.

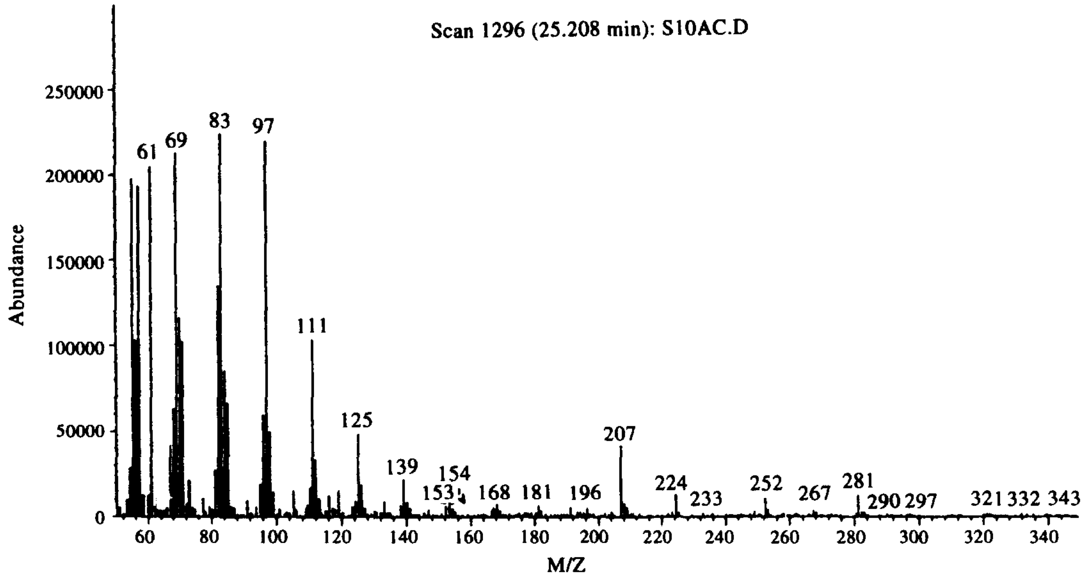

**Fig. 4.** E.i.–m.s. of peak with $t = 25{\cdot}2$ min in Fig. 3a.

## DISCUSSION

It is harder to substitute cellulose with large alkyl groups than with small ones. This is not surprising, because a large reagent molecule would diffuse more slowly into the swollen fibres than a small one. The plausibility of this explanation may, however, obscure other effects that are at least as important.

None of the higher, 1,2-epoxyalkanes tested in this work reacted significantly with cellulose under conditions that would have led to fairly high DS with 1,2-epoxyethane as the reagent (Klug & Tennent, 1951; Klug, 1963). Part of the explanation may be that primary hydroxyls are substituted much faster than secondary ones. This would allow the side-chains to grow much faster with 1,2-epoxyethane (to give polyethyleneglycol chains) than with higher 1,2-epoxyalkanes. It would also mean that the solvent (*iso*propanol) would consume epoxide at about the same rate as the cellulose when the higher homologues are used.

Alkyl iodides are excellent, but expensive, alkylating agents. With butyl iodide, a DS of 0·5 was achieved in a single operation with 1·1 mol of reagent per mole of hydroxyl group. Under our experimental conditions, methyl iodide would not give a much better final DS than this, though it would probably react faster.

With the alkyl bromides, useful DS values were achieved in most cases. As expected, there was a strong dependence of DS upon reaction time, but the kinetics were complex. There were indications of an auto-acceleratory effect, that is, an increase in rate of substitution with increasing DS. With octyl bromide, for example, there was no significant substitution after 3 h (S17), but the DS reached 0·11 after 25 h (S18). With octadecyl bromide, the DS reached 0·10 after 26 h (S19), but 0·30 after 72 h (S13).

Auto-acceleratory effects are well known in cellulose chemistry. In the periodate oxidation of cellulose I, for example, the rate of reaction increases markedly at two separate stages. The first is believed to correspond to a breakdown in the crystal structure of the microfibrils, leading to an increase in accessibility; while the second corresponds to the onset of depolymerisation, catalysed by hydroxy-radicals (Painter, 1988). The first stage should also occur for substitution reactions, and when these are carried out in alkaline media in the presence of atmospheric oxygen, the second should occur also (Ott *et al.*, 1954).

The notion that the rate of substitution should decrease with increasing size of the reagent molecule is not consistently supported by our data. For example, octyl bromide (S18) and octadecyl bromide (S19) gave similar DS values under similar conditions, as did dodecyl and hexadecyl bromides (S14 and S16, respectively). Likewise, there was no correlation between chain length and DS for the series tetradecyl : hexadecyl : octadecyl (S12, S11 and S10, respectively). Possibly these findings can also be understood in terms of auto-acceleratory effects. A large alkyl substituent may disrupt the microcrystallites more than a small one, and a hydrophobic substituent should make the cellulose more accessible to a hydrophobic reagent molecule.

The reagent prepared by dissolving sodium hydride in DMSO appeared to be a significantly better catalyst than sodium hydroxide in the same solvent. This may be because the hydride would dry the DMSO completely by reacting with any trace of moisture that it may contain or absorb from the atmosphere during the

**Table 4. Results of elemental and IR spectroscopic analysis**

| Derivative | Formula and $M_W$ of the mono-substituted anhydro-D-glucose repeat unit | | Calculated (%) | | | Found (%) | | | $H_2O$ (%) | $DS_{EA}$ | R | $A_{IR}$ | $DS_{IR}$ (OH/CH) | $DS_{IR}$* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | O | C | H | O | | | | | | |
| Cellulose | $C_6H_{10}O_5$ | 162·146 | 44·45 | 6·22 | 49·33 | 42·0 | 6·02 | 45·5 | 6·9 | — | 3/7 | 11·00 | — | — |
| S1 | $Cc_{10}H_{18}O_6$ | 234·254 | 51·27 | 7·75 | 40·98 | 42·3 | 6·13 | — | 5·3 | 0·06 | 3/15 | 10·15 | 0·07 | 0·05 |
| S2 | " | " | " | " | " | 41·4 | 6·02 | — | 5·3 | 0·00 | " | 9·73 | 0·11 | 0·08 |
| S3 | " | " | " | " | " | 41·5 | 6·05 | | 5·3 | 0·00 | " | 10·22 | 0·07 | 0·04 |
| S4 | $C_{14}H_{26}O_6$ | 290·362 | 57·91 | 9·03 | 33·06 | 42·4 | 6·15 | | 8·0 | 0·09 | 3/23 | 10·24 | 0·03 | 0·02 |
| S5 | " | " | " | " | " | 40·7 | 5·94 | — | 5·3 | 0·00 | " | 10·50 | 0·02 | 0·01 |
| S6 | $C_{16}H_{30}O_6$ | 318·416 | 60·35 | 9·50 | 30·15 | 41·9 | 6·06 | — | 5·3 | 0·01 | 3/27 | 10·97 | < 0·01 | < 0·01 |
| S7 | $C_{10}H_{18}O_5$ | 218·254 | 55·03 | 8·31 | 36·66 | 48·0 | 7·11 | 40·2 | 4·6 | 0·50 | 2/16 | 5·07 | 0·58 | 0·44 |
| S8 | $C_{24}H_{46}O_6$ | 430·632 | 66·94 | 10·77 | 22·29 | 41·8 | 6·09 | | 5·0 | < 0·01 | 3/43 | 10·94 | < 0·01 | < 0·01 |
| S9 | " | " | " | " | " | 42·3 | 6·16 | — | 5·3 | 0·01 | " | 7·94 | 0·07 | 0·05 |
| S10 | $C_{24}H_{46}O_5$ | 414·632 | 69·57 | 11·18 | 19·25 | 53·4 | 8·10 | 34·2 | 4·3 | 0·24 | 2/44 | 3·53 | 0·33 | 0·24 |
| S11 | $C_{22}H_{42}O_5$ | 386·578 | 68·35 | 10·95 | 20·70 | 49·7 | 7·50 | — | 5·3 | 0·18 | 2/40 | 4·64 | 0·25 | 0·17 |
| S12 | $C_{20}H_{38}O_5$ | 358·524 | 67·00 | 10·68 | 22·32 | 52·4 | 8·08 | — | 4·4 | 0·29 | 2/36 | 3·67 | 0·39 | 0·28 |
| S13 | $C_{24}H_{46}O_5$ | 414·632 | 69·57 | 11·18 | 19·25 | 53·7 | 8·45 | — | 5·3 | 0·30 | 2/44 | 3·25 | 0·37 | 0·26 |
| S14 | $C_{18}H_{34}O_5$ | 330·470 | 65·42 | 10·37 | 24·21 | 46·6 | 6·90 | 41·0 | 6·8 | 0·14 | 2/32 | 6·73 | 0·15 | 0·11 |
| S15 | $C_{20}H_{38}O_5$ | 358·524 | 67·00 | 10·68 | 22·32 | 43·3 | 6·40 | — | 5·3 | 0·04 | 2/36 | 8·63 | 0·06 | 0·04 |
| S16 | $C_{22}H_{42}O_5$ | 386·578 | 68·35 | 10·95 | 20·70 | 46·8 | 7·11 | — | 5·3 | 0·12 | 2/40 | 6·55 | 0·13 | 0·09 |
| S17 | $C_{14}H_{26}O_5$ | 274·362 | 61·29 | 9·55 | 29·16 | 41·5 | 6·00 | — | 3·7 | 0·00 | 2/24 | 9·87 | 0·04 | 0·03 |
| S18 | " | " | " | " | " | 44·8 | 6·43 | — | 5·3 | 0·11 | " | 6·17 | 0·26 | 0·18 |
| S19 | $C_{24}H_{46}O_5$ | 414·632 | 69·57 | 11·18 | 19·25 | 47·1 | 7·01 | — | 5·1 | 0·10 | 2/44 | 5·18 | 0·19 | 0·13 |
| S20 | $C_{20}H_{38}O_5$ | 358·524 | 67·00 | 10·68 | 22·32 | 49·9 | 7·59 | — | 4·3 | 0·20 | 2/36 | 3·78 | 0·37 | 0·27 |

*See text for explanation.

reaction. The NaH–DMSO reagent seemed, however, to cause more depolymerisation than NaOH–DMSO, because the products had lost much more of the fibrous appearance of the original cellulose. A special study of the effect of reaction conditions upon molecular weight is needed to clarify this point.

The development of reliable methods of analysis was a prerequisite for this project, and the discussion above is based entirely upon the data collected in Table 4. The method based on elemental analysis is straightforward, though special care is needed in measuring and correcting for the moisture contents of the samples. The method based upon IR spectroscopy is reasonably well-founded. For unsubstituted cellulose, the main IR-absorption bands were completely assigned approximately 20 years ago (Blackwell, 1977), and recent progress with second-derivative spectra is reported by Michell (1993). The quantitative use of IR-spectroscopic data is complicated theoretically by the fact that the wavelengths and intensities of the vibrational transitions are somewhat influenced by the chemical environments of the linkages concerned. It is straightforward when the absorbance is high and the chromophores are present in chemically similar moieties (Turunen *et al.*, 1969). The present results suggest that the method can be successfully used for cellulose ethers, provided it is calibrated by an independent method such as elemental analysis.

Chromatography (TLC and GLC) of the acetolysis products and mass spectrometry of a few of them demonstrated qualitatively but convincingly that these derivatives were alkyl ethers of cellulose, and not merely alkanols physically occluded by cellulose. The method was, however, not well suited for quantitative determination of DS values, because this would require correction for losses due to acid-catalysed dehydration reactions. A separate correction factor would be needed for each sugar and alkyl ether, and the problems in determining these accurately would be formidable. Methanolysis and hydrolysis were also tried as alternative methods of depolymerisation, but the problems were the same.

Without doubt, these derivatives can be validly described as 'hydrophobic'. Those with $DS > 0{\cdot}2$ floated on water and swelled up in organic solvents, in which a few of them partly dissolved. The derivatives also absorbed less methylene blue than unsubstituted cellulose that had been treated in the same reaction medium. The crystal structures and other physical properties will be dealt with in later papers.

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