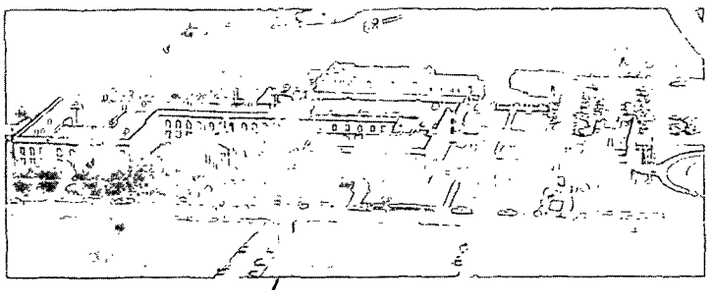

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# CARBOXYMETHYLATION AND METHYLATION OF CELLULOSE IN THE DIMETHYL SULFOXIDE/PARAFORMALDEHYDE SOLVENT SYSTEM

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## INTRODUCTION

Earlier, we reported the discovery of a new solvent system which dissolves cellulose without degradation (IPC Technical Paper Series Number 5). The solvent system, DMSO/PF, holds considerable promise of wide utility in cellulose technology. Its use in viscosity studies has been reported (IPC Technical Paper Series Number 8). Applications of possible commercial interest include regeneration of dissolved cellulose in the form of fibers and films, blends of cellulose with synthetic polymers and the production of cellulose derivatives.

The present paper is the result of Institute thesis research and demonstrates that carboxymethyl cellulose and methyl cellulose can be prepared in the solvent system. Furthermore, these derivatives can have a distribution of substituents on the cellulose hydroxyl groups that is markedly different from conventional preparations. Unusual cellulose acetals can be produced. The cellulose solvent system clearly provides a new route to novel cellulose derivatives.

The work described herein is being presented at the 1976 Canadian Wood Chemistry Symposium at Mont Gabriel, Quebec. It will be submitted for publication in Cellulose Chemistry and Technology.

# CARBOXYMETHYLATION AND METHYLATION OF CELLULOSE IN THE DIMETHYL SULFOXIDE/PARAFORMALDEHYDE SOLVENT SYSTEM

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Myron D. Nicholson and Donald C. Johnson*

## ABSTRACT

Carboxymethylation and methylation of cellulose was achieved in the dimethyl sulfoxide/paraformaldehyde (DMSO/PF) cellulose solvent system. The resulting carboxymethyl cellulose possessed a limiting low degree of substitution (DS) of about 0.20 while methyl cellulose samples could be prepared over a wide range of DS levels. Analysis of the cellulose ethers indicated preferential substitution at the secondary hydroxyl groups (C-2 and C-3). Both carboxymethylation and methylation supported the view that methylol groups (formed during dissolution of cellulose in DMSO/PF) were located mainly on the primary C-6 hydroxyl groups. These methylol groups permit the formation of acetal as well as ether linkages under certain conditions of cellulose etherification. The methylol groups act as blocking groups (with respect to etherification), and their influence on cellulose etherification was found to be dependent on the reaction conditions. Thus, it was possible to achieve a significant degree of control over the substituent distribution produced in cellulose etherification.

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# INTRODUCTION

We have recently reported that cellulose can be dissolved in dimethyl sulfoxide (DMSO) containing less than 1% of dissolved paraformaldehyde (PF) (1). This solvent system was shown to be nondegrading in nature (2) and was capable of dissolving a wide variety of cellulosic materials. Complete recovery of the cellulose from solution (DMSO/PF) was easily achieved by dilution with water or alcohol.

Evidence presented in the preceding paper illustrated that the formation of methylol cellulose, a hemiacetal, was critical to the overall success of the dissolution. This important reaction of cellulose with formaldehyde in the presence of DMSO (Fig. 1) was shown feasible by NMR analysis and was further substantiated by isolation and characterization of the methylol cellulose derivative. The DMSO has at least two important roles in the solvent system; one is to promote swelling of the cellulose thus facilitating reaction with formaldehyde and, second, is the stabilization of the hemiacetal via hydrogen-bonding association.

In the present work, our major goal was to examine homogeneous etherification reactions of cellulose in the DMSO/PF solvent with the intent of determining relative reactivity of hydroxyl groups and of gaining improved control over such reactions. It was recognized that the presence of attached methylol groups might have an important impact on the course of these reactions. The etherifications studied were carboxymethylation and methylation. Substituent group distributions were obtained by hydrolysis of the modified cellulose followed by quantitative gas-liquid chromatography (g.l.c.) of the resulting etherified glucose derivatives.

## EXPERIMENTAL

### Cellulose Solutions

The procedure employed to prepare cellulose solutions was a slight modification of that reported earlier (1). Cellulose powder (15 g, Whatman CF-1) was suspended in dimethyl sulfoxide (473 ml), and the slurry was stirred and heated to 120°C. Then, paraformaldehyde (30 g, Mallinckrodt, 95%, photographic grade) powder was added. A vigorous evolution of formaldehyde gas ensued. The cellulose completely dissolved within 15 minutes forming DMSO-soluble methylolcellulose. The temperature was allowed to increase to about 130° to decompose excess paraformaldehyde. Other commercial samples of paraformaldehyde (for example, Fluka PF) could be used successfully provided that they readily decomposed to formaldehyde at temperatures below 130°C.

### Preparation of Carboxymethyl Cellulose (CMC)

Sodium hydride (6 g, 0.250 mole) was slowly added to 100 ml of the above methylol cellulose solution containing ca. 3 g cellulose (0.019 mole). The reaction mixture was mechanically stirred at 19°C and within 1 hr became gel-like. After 2 hr, methyl bromoacetate (7 ml, 0.076 mole) was added dropwise over 1-2 hr. As the reaction proceeded, the gel dissolved followed by a later precipitation of the CMC. Total reaction time was 16-20 hr at 19°C. The degree of substitution (DS) of the CMC obtained ranged from 0.14-0.21 and appeared to be limited to that DS at which the product became DMSO-insoluble. The higher DS (0.21) was achieved using a reaction temperature of 50°C. A second treatment of the precipitated CMC with sodium hydride and methyl bromoacetate did not change the DS significantly.

Upon completion of the reaction, excess sodium hydride was decomposed by pouring the reaction mixture slowly into a vigorously stirred formic acid: water (1:1, v/v) solution (250 ml). The resulting aqueous slurry (pH 3-4) of CMC

containing the by-products of reaction was dialyzed against distilled water using an Amicon apparatus at 12-15 p.s.i.g. nitrogen. The dialysis unit was equipped with a XM 50 membrane capable of retaining molecules greater than 50,000 molecular weight. Dialysis continued until the slurry was neutral (pH 7) or until at least six volumes of the original slurry had been exchanged (ca. 24 hr). The purified aqueous suspension of CMC was freeze-dried to give 2.95 g of material. The infrared spectrum contained a band at 1730 $cm^{-1}$ confirming the presence of the acid form of CMC rather than the methyl ester.

## Preparation of Methyl Cellulose (MC)

Sodium hydride (2 g) was stirred into 50 ml of a methylol cellulose solution containing 1.5 g cellulose. After 2 hr at 19°C the solution had taken on a gel-like appearance. With constant stirring, methyl iodide (3 ml) was slowly added. Within minutes the gel dissolved and the reaction was allowed to continue 24 hr.

Three such successive sodium hydride/methyl iodide treatments were employed. Methyl celluloses of varying degrees of substitution (DS) were obtained after each treatment. Purification began by pouring the reaction mixture slowly into a formic acid:water (1:1, v/v) solution (100 ml). The resulting solution was dialyzed employing the same dialysis unit and conditions as cited for the CMC purification. In cases where a high DS (water insoluble) ether was isolated, the dialysis time was increased. The purified solution (DS < 2) or slurry (DS > 2) of methyl cellulose was freeze-dried.

## Preparation of Carboxymethylmethylol Cellulose Methyl Ester (CMMOLC)

Methyl chloroacetate (1 ml) was added to a methylol cellulose solution (20 ml) containing ca. 0.6 g cellulose. This carboxymethylating reagent was chosen so that upon freeze-drying excess reagent could be removed. The reaction mixture was stirred continuously while adding 20 drops (ca. 0.2 ml) of triethylamine. This

reaction was allowed to proceed 22 hr at 23°C. Since the products of reaction remained DMSO-soluble, purification was by freeze-drying, redissolution in DMSO and freeze-drying a second time.

The infrared spectrum of the product contained a band at 1745 $cm^{-1}$ characteristic of CMC methyl ester substituents but no detectable band at 1760 $cm^{-1}$ indicating complete removal of excess methyl chloroacetate. Analysis by gas-liquid chromatography (described below) of the product hydrolyzate after acid-catalyzed hydrolysis revealed only the presence of glucose but no significant amounts of carboxymethyl glucoses. The reaction product was concluded to be carboxymethylmethylol cellulose methyl ester (CMMOLC) where the added carboxymethyl groups are bonded via acetal rather than ether linkages.

## Analytical Procedures

### Hydrolysis

All cellulose derivatives were hydrolyzed prior to gas-liquid chromatographic (g.l.c.) analysis according to the procedure of Croon and Purves (3). Upon completion, the hydrolyzate was neutralized (pH 7) with barium carbonate and the insoluble barium salts were removed by filtration. The resulting aqueous solution was concentrated to dryness *in vacuo* at 50°C.

### Esterification/glycosidation

The dry residue remaining after CMC hydrolysis was subjected to a Fischer esterification/glycosidation employing 4% HCl/methanol under reflux conditions for 24 hr. The methanolic HCl was prepared by slow addition of acetyl chloride (7 ml) to anhydrous methanol (100 ml). Upon completion of the esterification/glycosidation, the HCl was neutralized with barium carbonate and the subsequent barium salts allowed to settle. The g.l.c. internal standard for quantitative glucose

(DS) analysis (methyl β-D-xylopyranoside) was added prior to refluxing, while the internal standard for carboxymethyl glucose analysis (cyclohexyl β-D-glucopyranoside) was added after neutralization of the HCl. An aliquot of the methanolic solution was concentrated to dryness in vacuo at 50°C prior to trimethylsilylation.

The methyl cellulose products were subjected to glycosidation as above except internal standards were not employed.

Trimethylsilylation and GLC Analysis

Trimethylsilylation (4) was accomplished by addition of TRI-SIL (Pierce Chemical Co.) to the dry sample with 1 ml of TRI-SIL used per 5-10 mg of carbohydrate. To facilitate sample dissolution and insure complete reaction, the reaction solution (TRI-SIL + sample) was heated 5-10 min. at 50°C. Reaction was allowed to proceed at 25°C for at least 12 hr with constant mechanical shaking. The reaction solution could be used directly for g.l.c. analysis of substituent distribution, but for glucose analysis it was necessary to remove the pyridine in vacuo and redissolve the residue in anhydrous di-isopropyl ether.

Analysis of the trimethylsilyl (TMS) derivatives by g.l.c. was accomplished using a Varian Aerograph 1200 instrument and a stainless steel column composed of 5% SE-30 on 60-80 mesh Chromosorb W (1/8 inch x 10 ft). The operating conditions for CMC hydrolyzate analyses were: column, programmed 210-250°C at 1° $min.^{-1}$; injector, 250°; detector, 270°; $N_2$ flow, 13 ml $min.^{-1}$. For MC hydrolyzate analyses the same conditions were used except: column, programmed 170-210° at 1° $min.^{-1}$; $N_2$ flow, 15 ml $min.^{-1}$.

Identification of the hydrolysis components detected by g.l.c. was made possible by comparison with known samples which included mass spectrometry. Each of the three monosubstituted carboxymethyl glucose components (2-O-CMgl, 3-O-CMgl and 6-O-CMgl) and selected methyl glucose components (2-O-Megl, 3-O-Megl and 2,3-di-O-Megl) were synthesized. Response factors for the volatile derivatives of the

carboxymethylglucoses were obtained using known mixtures with an internal standard, cyclohexyl β-D-glucopyranoside. The three factors were almost identical.

Mass Spectrometry

For mass spectrometric analysis, it was necessary to use the silylated ethyl ester/glycoside derivatives in order to eliminate the mass equality of TMS ether and carboxymethyl methyl ester substituents. These derivatives were prepared using the above esterification/glycosidation procedure except that 4% HCl/ethanol was employed. As anticipated (5-8), the isomeric monocarboxymethyl glucose derivatives produced different mass spectra. The H-, F- and J-fragmentation pathways (6) were of greatest value in confirming location of the substituents.

## Synthesis of Reference Materials

Methyl 2-O-carboxymethyl-D-glucopyranoside, methyl ester (2-O-CMgl)

Using the procedure of Finan and Warren, 1,2-O-isopropylidene-α-D-glucofuranose (9) was completely benzylated (10). The resulting tribenzyl derivative was purified by column chromatography employing a 1m. silica gel (60-200 mesh) column and isopropyl ether as the eluant. This purified material was methanolyzed in 4% HCl/methanol under reflux conditions 26 hr. The product, methyl 3,5,6-tri-O-benzyl-D-glucofuranoside, was purified by column chromatography (silica gel, isopropyl ether:benzene, 10:1) and carboxymethylated according to the procedure of Shyluk and Timell employing sodium hydride and methyl bromoacetate (11). Removal of the benzyl groups by catalytic hydrogenation [10% palladium on charcoal (12) and 40 p.s.i.g. hydrogen] followed by column purification (silica gel, chloroform: methanol, 10:1) yielded the desired compound, 2-O-CMgl which possessed $[\alpha]_D^{25}$ + 33.3° (c 1, MeOH). It was shown to be pure by g.l.c. and thin-layer chromatographic (t.l.c.) analysis. The location of the 2-O-carboxymethyl group was confirmed by mass spectral analysis of the analogous silylated ethyl ester/glycoside. Substantial peaks for fragment ions at m/e 231 and 218 (base) represented the $F_1^2$ and $H_1^2$ fragmentation routes, respectively.

Methyl 3-O-carboxymethyl-D-glucopyranoside, methyl ester (3-O-CMgl)

According to the basic procedure of Shyluk and Timell, 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (13) was carboxymethylated (11). The isopropylidene groups were subjected to methanolysis by refluxing (24 hr) a methanol (100 ml) suspension containing the isopropylidene derivative (7 g) and Amberlite IR-120 ion-exchange resin (20 ml) which had previously been solvent-exchanged by replacing water with methanol. After removal of the resin by filtration, the methanol solution was concentrated in vacuo at 50°C and purified by column chromatography employing silica gel and chloroform:methanol (10:1) eluant. This purified material (3-O-CMgl) had $[\alpha]_D^{25}$ + 63.6° (c 1.45, MeOH). Purity was confirmed by g.l.c. and t.l.c. The location of the 3-O-carboxymethyl group was confirmed by mass spectral analysis. The analogous silylated ethyl ester/glycoside gave major fragment ions at m/e 218 (base), 217 and 161 representing the $H_1^2$, $F_1^2$, and $J_1$ routes, respectively.

Methyl 6-O-carboxymethyl-D-glucopyranoside, methyl ester (6-O-CMgl)

The selectively blocked material, 6-O-acetyl-bismethylene-D-glucofuranose, was prepared according to the procedure of Hough, Jones and Magson (14). Deacetylation was accomplished in 1N methanolic sodium methoxide. The resulting reaction mixture was deionized (Amberlite MB-3) prior to concentration in vacuo. The resulting sirup was carboxymethylated (11). Methanolysis of the methylene groups was achieved using methanol and IR-120 resin as cited above except refluxing was continued for 48 hours. The product was purified by column chromatography (silica gel, chloroform:methanol 10:1). The material possessed $[\alpha]_D^{25}$ + 70.1° (c 1.15, MeOH). The mass spectrum of the analogous ethyl ester/glycoside contained major fragment ions at m/e 217 and 204 (base) for the $F_1^2$ and $H_1^2$ routes.

Methyl 2-O-methyl, 3-O-methyl and 2,3-di-O-methyl-β-D-glucopyranoside mixture (2-O-Megl, 3-O-Megl, 2,3-di-O-Megl)

The desired selectively blocked material was obtained by debenzoylating methyl 2,3-di-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (15) (1 g) with 1N methanolic

sodium methoxide (50 ml) at 25°C. After the reaction was completed (12 hr), the product was crystallized in water (16). Methylation of this 4,6-O-benzylidene-β-D-glucopyranoside followed the procedure of Seib employing silver oxide, methyl iodide in dimethyl formamide (17,18). After 10 hr reaction, the methylation was quenched and the products extracted with chloroform. The mixture of methylated sugars was treated with methanolic HCl (4% HCl) under reflux (12 hr) which accomplished the removal of the benzylidene grouping. This product mixture was silylated and used to aid in identification of peaks in chromatograms containing methyl glycoside/TMS derivatives of the hydrolysis products from various methyl celluloses having a wide range of DS values. The identification was assisted further by the availability of known 3-O-methyl glucose (19).

## RESULTS AND DISCUSSION

### Carboxymethylation

Carboxymethylation of cellulose in solution (homogeneous) was attempted in the DMSO/PF system via two routes: (a) employing triethylamine and chloroacetic acid (or its methyl ester) and (b), using sodium hydride in conjunction with methyl bromoacetate.

Route (a) did not produce the desired etherification, but rather, acetalation of the methylol hydroxyl groups. This was demonstrated by hydrolysis of the carboxymethylated product to glucose without significant amounts of O-carboxymethyl glucoses. Carboxymethyl ethers of the cellulose were formed when sodium hydride and methyl bromoacetate [route (b)] were employed at reaction temperatures ranging from 19-50°C.

Analysis of methylolcellulose (1) showed about one methylol group for each anhydroglucose unit. Their high reactivity to acetalation was circumvented by use of sodium hydride which apparently promoted partial loss of methylol groups as shown.

$$\text{Cell-O-CH}_2\text{OH} + \text{NaH} \rightarrow \text{Cell-O}^-\text{Na}^+ + \text{CH}_2\text{O}$$

The degree of substitution of CMC prepared from methylol cellulose (MOLC) was limited to about 0.21 as shown in Table I. The limitation appeared to be due, at least in part, to insolubility of the CMC salt which inhibited further reaction. Although many cellulose ethers are DMSO-soluble, CMC (0.8 DS) has been reported to be insoluble (20). Methyl bromoacetate was chosen for the etherification since the CMC methyl ester was known to be DMSO-soluble, but the final product did not retain the ester group.

[Table I here]

The reaction with sodium hydride resulted in the reaction solution becoming gel-like. Then, as the etherification (with methyl bromoacetate) proceeded, the gel dissolved only to be followed (after 12 hr) by formation of a precipitate of the salt form of CMC.

The carboxymethyl cellulose prepared in DMSO/PF was analyzed to determine the distribution of substituents on the three hydroxyl groups. The CMC was first subjected to acid-catalyzed hydrolysis. Volatile derivatives for g.l.c. analysis were prepared by an esterification/glycosidation (methanol and acid) treatment followed by trimethylsilylation. The relative amounts of the carboxymethyl glucoses, 2-O-CMgl, 3-O-CMgl, and 6-O-CMgl, were determined by quantitative analysis with help of an internal standard (21). The mole ratios reflecting relative reactivity of the three hydroxyl groups are shown, for various reaction systems, in Table I. The chromatograms are included in Fig. 2. Systems studied include the carboxymethylation products of the hemiacetal methylol cellulose (MOLC) at 19 and 50°C and the acetal carboxymethylmethylol cellulose methyl ester (CMMOLC).

[Fig. 2 here]

The low substitution at the C-6 primary hydroxyl is seen in the first chromatogram (Fig. 2a). From Table I it can be seen that the C-2 and C-3 secondary hydroxyl

groups are about 1.5 times as reactive as the C-6 hydroxyl group. The reduction in the C-6 carboxymethylation reflects the preferential location of the methylol groups at the C-6 oxygen. With this site preferentially covered by methylol units, a greater possibility exists for etherification of the C-2 and C-3 hydroxyl groups. This was observed (chromatogram a).

Chromatogram b illustrates that C-6 substitution does increase markedly at the reaction temperature of 50°C. At 50°C almost uniform substitution is realized on the three hydroxyl groups. These results may be due to the removal of more methylol groups at this increased temperature providing more C-6 cellulose hydroxyl groups free to form the ethers.

Chromatogram c in Fig. 2 illustrates the component distribution obtained upon carboxymethylation of the acetal, carboxymethylmethylol cellulose methyl ester (CMMOLC), at 19°C. The stabilization of the methylol groups by acetal formation has a dramatic effect upon the subsequent C-6 etherification. Since this acetal is not cleaved by sodium hydride, the etherification was directed primarily to the C-2 and C-3 hydroxyls which are not methylolated to a substantial degree.

This observation of position-directed etherification provides evidence that the methylol groups responsible for cellulose dissolution in DMSO/PF are primarily located on the C-6 hydroxyl groups. The observed reduction in C-2 carboxymethylation (Fig. 2c) of the blocked acetal derivative may indicate limited attachment of methylol groups at the C-2 hydroxyl group. It has been reported in cellulose cross-linking reactions with formaldehyde that the primary C-6 hydroxyl groups are 10-20 times as reactive as the secondary hydroxyls (22).

Figure 2 thus illustrates the feasibility of controlling etherification reactions with cellulose in DMSO/PF. Either one can achieve uniform substituent

distribution between the 2,3, & 6 hydroxyls (at 50°C) or direct the etherification to the secondary C-2 and C-3 hydroxyl positions (at 19°C).

Table II provides a comparison of substituent distributions of CMC samples prepared in various ways. It is clear that the substituent distribution of CMC prepared in DMSO/PF is quite different from conventional CMC samples prepared by heterogeneous etherification (3). The relatively higher reactivity of the 3-hydroxyl in the DMSO/PF system is noteworthy.

[Table II here]

Carboxymethylation was also achieved in another solvent system which involved the dissolution of cellulose in an amine oxide, N-methylmorpholine-N-oxide, followed by dilution with DMSO (23). The relative amounts of N-oxide to DMSO were 1:9 by weight. Carboxymethylation was achieved as before using methyl chloroacetate and sodium hydride at 70°C. In this case, the etherification was directed primarily to the 6-position. This result serves to further underscore the importance of the methylol group in controlling cellulose etherification in the DMSO/PF system.

Methylation

Further support for the conclusions drawn from the carboxymethylation study was sought by a related study of methylation. Sodium hydride was again employed, and methyl iodide was the etherifying agent. Contrary to the prior etherification where DMSO-insolubility limited further reaction, methylation proceeded in a homogeneous system. By varying the reaction time and the number of sodium hydride/methyl iodide treatments, methyl cellulose samples of widely different DS levels (below one to nearly three) could be obtained.

Although the response factors for the various methyl glucose ethers were not determined, semiquantitative comparison to the carboxymethyl system was based upon the relative component g.l.c. peak areas. Since the molar responses of the

three monosubstituted carboxymethyl glucose derivatives are very similar, it is likely that responses of the three monosubstituted methyl glucose derivatives are likewise similar.

In an effort to look at a low DS methyl cellulose, which would be comparable to the CMC prepared in DMSO/PF, a sample was taken very early during the multistep methylation. After work-up (hydrolysis, methyl glycosidation and trimethylsilylation), chromatogram a was obtained (Fig. 3). Once again 6-O-etherification (peak E) is substantially lower than that resulting at the other two hydroxyl groups. It is concluded that the methylol group, located mainly at the C-6 oxygen, is controlling the extent of methylation of the various alcohol groups just as it does in carboxymethylation. At an intermediate stage of methylation (chromatogram b) the amount of di-O-methyl glucoses is considerably greater, but the relative order of the monomethyl glucoses (peaks C, D, and E) is not changed greatly from chromatogram a. The final chromatogram (c) illustrates the potential for removing virtually all of the methylol groups to obtain a methyl cellulose having a DS close to 3.0.

[Fig. 3 here]

The methylation is illustrated in Fig. 4 suggesting that both ether and acetal formation are competitive depending on the number of methylol groups present.

[Fig. 4 here]

## CONCLUSIONS

Homogeneous etherification of cellulose, employing both carboxymethylation and methylation, was accomplished in the DMSO/PF solvent. Analysis of the cellulose ethers obtained illustrated that the methylol substituent markedly influenced the course of etherification. Partial removal of methylol groups by increased reaction temperature (from 19 to 50°C) resulted in an increased O-6 substitution, while retention of methylol groups by acetal formation prior to etherification allowed a

relatively high O-2 and O-3 substitution. The data support the conclusion that the methylol groups were preferentially located at the primary C-6 hydroxyl position.

The use of methylol groups to direct the course of cellulose reactions provides a route to novel cellulose derivatives. Application of this route to other cellulose reactions appears feasible.

## ACKNOWLEDGMENTS

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TABLE I

ANALYSIS OF CMC PREPARED IN DMSO/PF

| Carboxymethylation of | Temp., °C | D.S. | Molar Ratio[a] of CM Ethers | | |
|---|---|---|---|---|---|
| | | | 2 | 3 | 6 |
| MOLC | 19 | 0.15 | 1.69 | 1.47 | 1.0 |
| MOLC | 50 | 0.21 | 1.11 | 1.0 | 1.21 |
| CMMOLC | 19 | (0.1-0.3)[b] | 6.51 | 9.36 | 1.0 |

[a]Each ratio is an average of three determinations using separate samples.
[b]Estimated by comparison with other chromatograms.

TABLE II

SUBSTITUENT DISTRIBUTIONS OF CMC SAMPLES

| Method of Preparation[a] | D.S. | Molar Ratios of CM Ethers | | |
|---|---|---|---|---|
| | | 2 | 3 | 6 |
| MOLC/DMSO/NaH, 19°C | 0.15 | 1.69 | 1.47 | 1.0 |
| MOLC/DMSO/NaH, 50°C | 0.21 | 1.11 | 1.0 | 1.21 |
| C/$H_2O$, IPrOH/NaOH[b] | 0.20 | 2.0 | 1.0 | 2.8 |
| Commercial | 0.37 | 2.02 | 1.0 | 1.55 |
| C/AmOx, DMSO/NaH | 0.45 | 1.0 | 1.4 | 4.0 |

[a] Various carboxymethylating agents were used.
[b] Croon and Purves, Svensk Papperstidn. 62:876(1959).

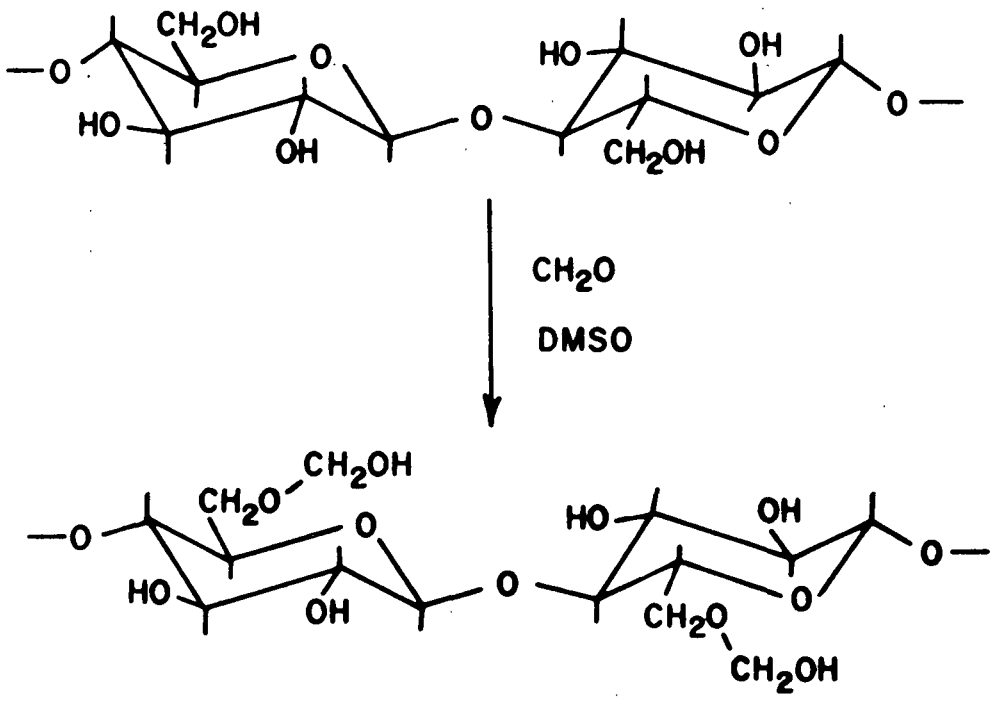


Fig. 1. Mechanism of Cellulose Dissolution in DMSO/PF: Formation of Methylol Cellulose

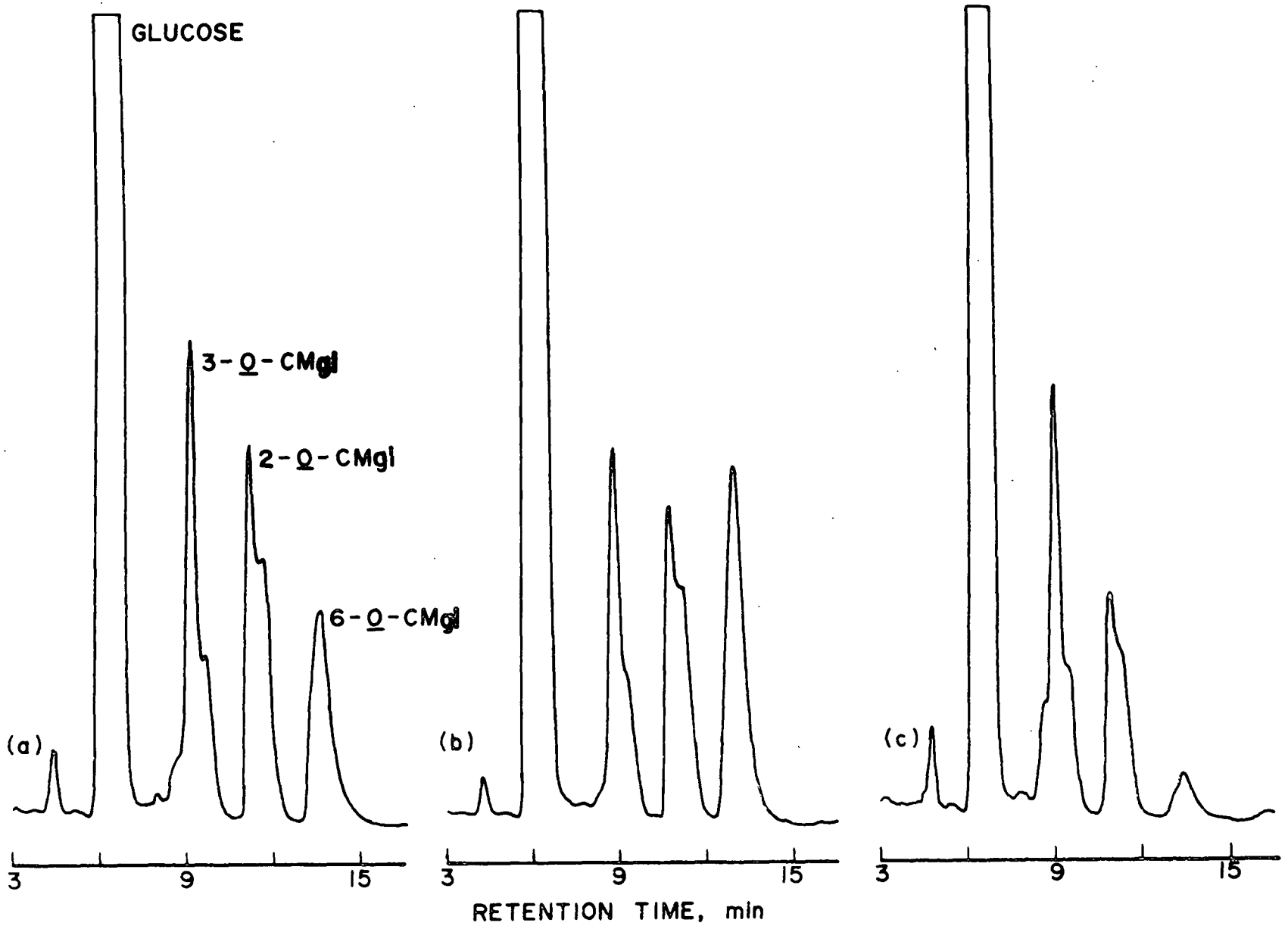


Fig. 2. Gas Chromatograms of Hydrolyzed Carboxymethyl Cellulose Prepared by Carboxymethylation of: a) Methylol Cellulose at 19°C, b) Methylol Cellulose at 50°C, and c) Carboxymethylmethylol Cellulose Methyl Ester at 19°C Showing Peaks for Glucose, 3-O-CMgl, 2-O-CMgl and 6-O-CMgl all as Methyl Ester/Methyl Glycoside Trimethylsilyl (TMS) Derivatives

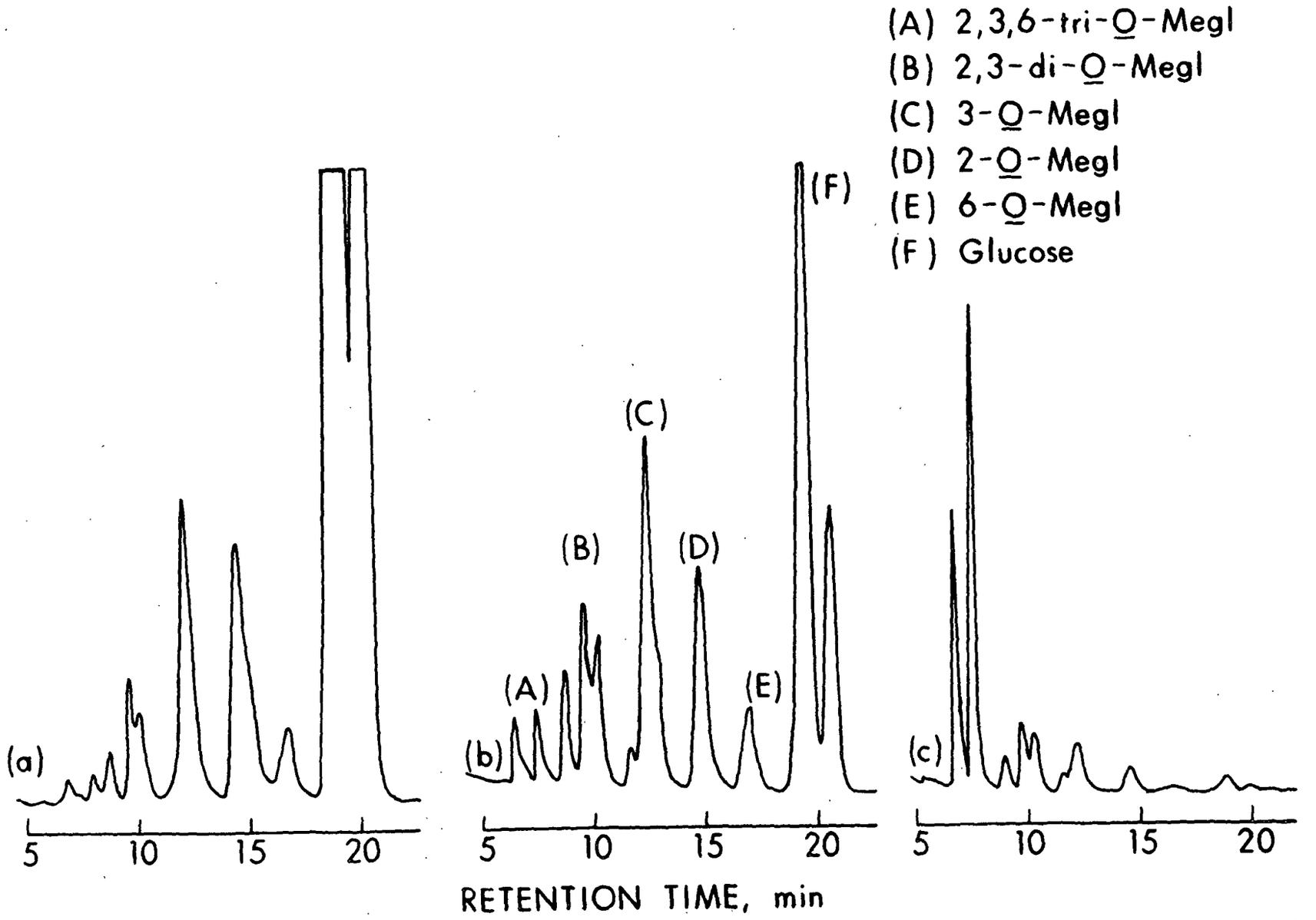


Fig. 3. Gas Chromatograms of Various Hydrolyzed Methyl Cellulose Samples Prepared in DMSO/PF at 20°C. Chromatogram (a) Sample DS <1, (b) DS >1, (c) DS >2; all Peaks as Methyl Glycoside TMS Derivatives

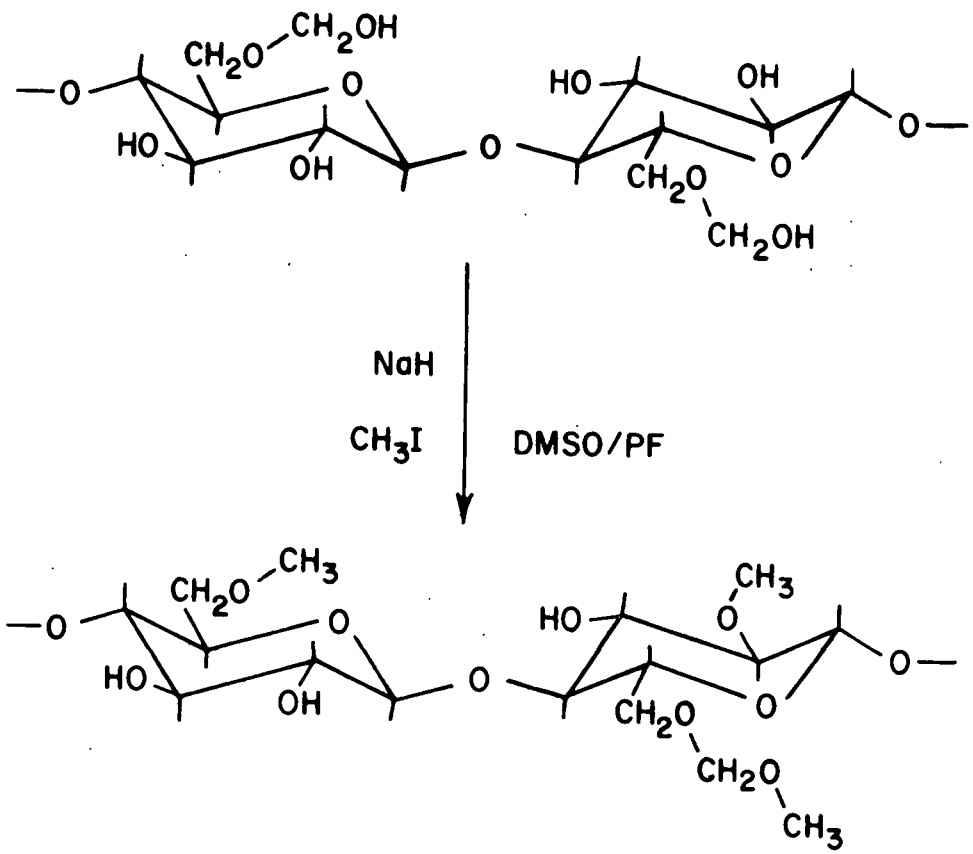


Fig. 4. Methylation of Methylol Cellulose in DMSO/PF