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ANALYSIS OF THE ^{13}C-N.M.R. SPECTRA OF HYDROLYZED AND METHANOLYZED *O*-METHYLCELLULOSES: MONOMER COMPOSITIONS AND MODELS FOR THEIR DESCRIPTION

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ABSTRACT

Complete assignments are presented of the ^{13}C-n.m.r. spectra of the mixtures of methylated D-glucoses and methylated methyl D-glucosides that respectively result from hydrolysis and methanolysis of commercial samples of *O*-methylcellulose. The effects of methylation on the ^{13}C chemical shifts of some of the atoms deviate from additivity, indicating interaction between the substituents at C-1, -2, and -3 of the D-glucopyranose ring. The monomer composition (given by the mole fractions of the component monosaccharides) conforms to a statistical, kinetic model that assumes that the reactivity of the 3-hydroxyl group depends upon the state of substitution at C-2. The relative rate-constants (averaged over the two samples) of the hydroxyl groups in the methylation reaction are $k_2:k_3:k_3':k_6$ = 1.24:0.28:0.82:1.00, indicating that the reactivity of OH-3 increases threefold upon methylation of OH-2.

INTRODUCTION

The determination of the monomer composition of partly substituted polysaccharide ethers is a challenging analytical task. The exploratory work of Parfondry and Perlin[1] on the ^{13}C-n.m.r. spectroscopy of cellulose ethers has shown that, in principle, information on the monomer composition is extractable from the spectra of the degraded (*e.g.*, hydrolyzed) polymers. Subsequently, Lee and Perlin analyzed the spectra of hydrolyzed[2] and methanolyzed[3] *O*-(hydroxypropyl)cellulose in terms of the degree of positional substitution. With the aid of separated monosaccharides, Reuben and Conner[4] fully assigned the spectrum of hydrolyzed *O*-(carboxymethyl)cellulose (CMC), and obtained the monomer composition of the polymer. They showed that the monomer composition of CMC is adequately described by a simple, statistical, kinetic model proposed by Spurlin[5] in 1939. This approach is now applied to *O*-methylcellulose (MC).

Manufacturing processes for the production of MC involve the heterogeneous reaction of alkali-cellulose with methyl chloride[6]. The reaction conditions are usually so chosen that the resulting product has an average degree of substitution

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(d.s.) in the range of 1.4–2.0. Therefore, the 2-, 3-, and 6-hydroxyl groups of the D-glucosyl residues of cellulose are, on the average, only partly substituted. Thus, similarly to CMC, MC may be regarded as a copolymer of eight monomers: residues of D-glucose, three *O*-methylglucoses (2-, 3-, and 6-), three di-*O*-methylglucoses (2,3-, 2,6-, and 3,6-), and 2,3,6-tri-*O*-methyl-D-glucose. Because of the inherent intra- and inter-chain heterogeneity of polymeric MC, analytical procedures for determination of its monomer composition involve hydrolysis of the material with acid[7,8]. In this way, a mixture of 16 monosaccharide species is formed, taking into account the α and β anomers of each of the eight monomers. The situation will be similar in the case of methanolysis. Thus, in the ^{13}C-n.m.r. spectrum of hydrolyzed MC, 120 lines, of 16 different intensities, are to be expected. There will be 136 lines in the spectrum of methanolyzed MC. Four of the monomeric sugars, namely, D-glucose, 3-*O*-methyl-D-glucose, 2,6-di-*O*-methyl-D-glucose, and 2,3,6-tri-*O*-methyl-D-glucose (and the corresponding methyl D-glucosides) were available for this work. Their spectra, and the literature data on the *O*-methyl-D-glucoses[9] and 2,3,4,6-tetra-*O*-methyl-D-glucose[10], were essential for making the spectral assignments of the mixtures. From the spectroscopist's point of view, the interest in the analysis of such mixtures lies in obtaining the substituent effects on carbon-13 chemical shifts in one experiment, thereby eliminating the influences of different experimental conditions. Data of this kind should be useful for spectral assignments of other, related derivatives, *e.g.*, degradation products of permethylated polysaccharides. The relative, integrated intensities of the spectral lines yield the mole fractions of the component monosaccharides, *i.e.*, the monomer composition. Theoretical models for description of the monomer composition of MC are summarized in the next section.

Theoretical models. — Spurlin's statistical, kinetic model[5] for description of the arrangement of substituents (monomer composition) in cellulose ethers involves the following assumptions. (*a*) All D-glucose residues are equally accessible for reaction. (*b*) Substitution within a given D-glucose unit does not affect the reactivity of the remaining hydroxyl groups. (*c*) The extent of substitution at each position is governed by the relative rates of reaction of the hydroxyl groups in a first-order process and the relative rate constants remain unchanged throughout the process. (*d*) The effect of end groups is negligible. However, because evidence on the monomer composition of some derivatives had indicated that the reactivities of the 2- and 3-hydroxyl groups were correlated, Spurlin[11] modified assumption (*b*) so as to read: "The only interference of substitution within a glucose unit occurs between positions 2 and 3". Thus, the following reactions must be considered.

$$\text{–C-6–OH} + \mathrm{CH_3Cl} \xrightarrow{k_6} \text{–C-6–OCH}_3 + \mathrm{HCl} \tag{1}$$

$$\text{–C-3–(OH)C-2–OH} + \mathrm{CH_3Cl} \xrightarrow{k_2} \text{–C-3–(OH)C-2–OCH}_3 + \mathrm{HCl} \tag{2}$$

$$-\mathrm{C\text{-}3\text{-}(OH)C\text{-}2\text{-}OH} + \mathrm{CH_3Cl} \xrightarrow{k_3} -\mathrm{C\text{-}3\text{-}(OCH_3)C\text{-}2\text{-}OH} + \mathrm{HCl} \tag{3}$$

$$-\mathrm{C\text{-}3\text{-}(OH)C\text{-}2\text{-}OCH_3} + \mathrm{CH_3Cl} \xrightarrow{k_3'} -\mathrm{C\text{-}3\text{-}(OCH_3)C\text{-}2\text{-}OCH_3} + \mathrm{HCl} \tag{4}$$

$$-\mathrm{C\text{-}3\text{-}(OCH_3)C\text{-}2\text{-}OH} + \mathrm{CH_3Cl} \xrightarrow{k_2'} -\mathrm{C\text{-}3\text{-}(OCH_3)C\text{-}2\text{-}OCH_3} + \mathrm{HCl} \tag{5}$$

For convenience, we define the probability functions

$$p_i = e^{-Bk_i}, \tag{6}$$

where k_i is a first-order rate-constant and B is a factor with the dimension of time. The solutions[11] of the first-order rate-equations written according to the kinetic scheme of Eqs. *1–5* give the following results for the mole fractions, s_i (the subscript indicates the positions of substitution), of the individual monomers.

$$s_0 = p_2p_3p_6 \tag{7}$$

$$s_2 = p_6M(p_3' - p_2p_3) \tag{8}$$

$$s_3 = p_6N(p_2' - p_2p_3) \tag{9}$$

$$s_6 = p_2p_3x_6 \tag{10}$$

$$s_{23} = p_6[1 - p_2p_3 - M(p_3' - p_2p_3) - N(p_2' - p_2p_3)] \tag{11}$$

$$s_{26} = x_6\,M(p_3' - p_2p_3) \tag{12}$$

$$s_{36} = x_6\,N(p_2' - p_2p_3) \tag{13}$$

$$s_{236} = x_6[1 - p_2p_3 - M(p_3' - p_2p_3) - N(p_2' - p_2p_3)], \tag{14}$$

where

$$M = k_2/(k_2 + k_3 - k_3'), \tag{15}$$

$$N = k_3/(k_2 + k_3 - k_2'), \text{ and} \tag{16}$$

$$x_i = 1 - p_i \tag{17}$$

Detailed analysis of a series of CMC samples has shown conclusively that, within experimental error, there is no correlation between the reactivities of the 2- and 3-hydroxyl groups[4]. On the other hand, data on laboratory preparations of MC could be fitted by assuming that only the reactivity of OH-3 increases when O-2 is methylated[7]. Therefore, for operational purposes, it is instructive to separate this general model into three different models. Model I, where $k'_2 = k_2$, $k'_3 = k_3$, $M = N = 1$, *i.e.*, no correlation; Model II, where $k'_2 = k_2$ and $N = 1$ but $k'_3 \neq k_3$ and $M \neq 1$, *i.e.*, only the reactivity of OH-3 depends upon the state of substitution at O-2; Model III, where $k'_2 \neq k_2$ and $k'_3 \neq k_3$, *i.e.*, complete correlation.

If a set of experimental data on the monomer composition (values of s_i) is available, the conformity to the three models can be tested in the following fashion.

Model I. Positional degrees of substitution are calculated as:

$$x_2 = s_2 + s_{23} + s_{26} + s_{236} \tag{18}$$

$$x_3 = s_3 + s_{23} + s_{36} + s_{236} \tag{19}$$

$$x_6 = s_6 + s_{26} + s_{36} + s_{236} \tag{20}$$

Values of p_i are calculated as:

$$p_i = 1 - x_i \tag{21}$$

Expectation values of s_i are calculated with the appropriately simplified version of Eqs. *7–14*.

Model II. The positional degrees of substitution x_2 and x_6 are calculated with Eqs. *18* and *20*, respectively. The other necessary quantities are obtained as

$$p_3 = (1 - x_2 + s_0 + s_6 - s_3 - s_{36})/2(1 - x_2) \tag{22}$$

$$M(p'_3 - p_2p_3) = s_2 + s_{26} \tag{23}$$

Model III. Only x_6 remains the same as in the simplified models and is calculated with Eq. *20*. The other necessary quantities are obtained as

$$p_2p_3 = s_0 + s_6 \tag{24}$$

$$N(p'_2 - p_2p_3) = s_3 + s_{36} \tag{25}$$

and $M(p'_2 - p_2p_3)$ is given by Eq. *23*.

Thus, the conformity of experimental data to the models can be readily tested without assumptions regarding the actual values of the relative rate-constants (as done in the past[12]).

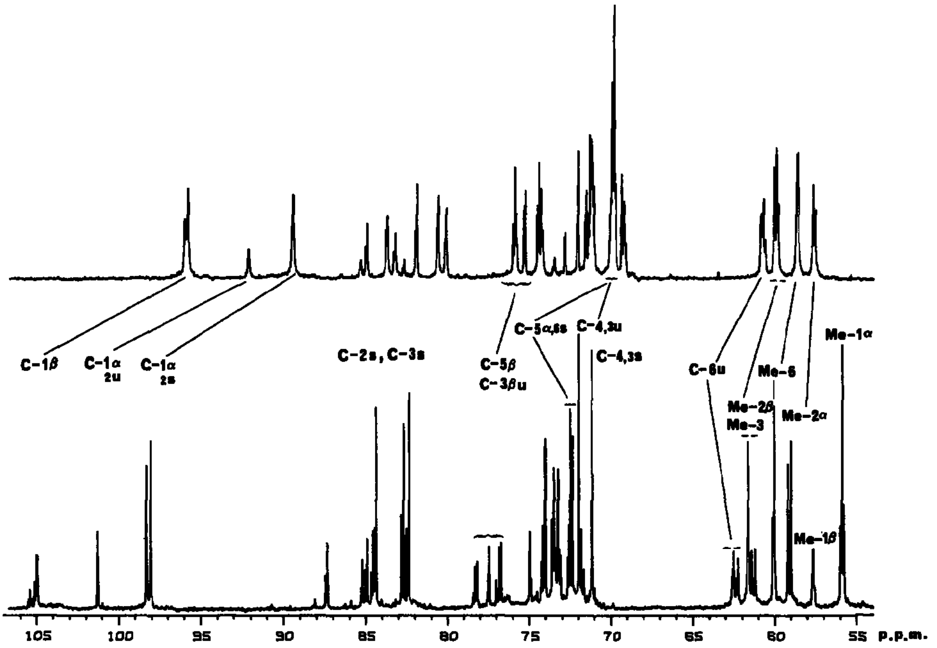
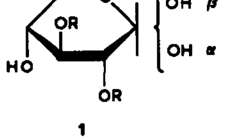


Fig. 1. ^{13}C-N.m.r. spectra of hydrolyzed (top) and methanolyzed (bottom) samples of *O*-methylcellulose. The letters s and u indicate substituted and unsubstituted, respectively.

RESULTS

Two commercial samples were investigated in this work. Sample A (Dow Methocell A15C Premium) was hydrolyzed. Hydrolysis of MC yields a mixture of 16 monosaccharide species. Included in the mixture are the anomers of D-glucose and a series of methylated D-glucoses described by formula **1**. The ^{13}C-n.m.r. spectrum of the mixture in acidified D_2O solution is shown in Fig. 1. Sample B (Henkel MC 4000) was insoluble in water; it was treated with methanolic HCl. Methanolysis of MC yields a mixture of 16 methyl glucosides described by formula **2**. The ^{13}C-n.m.r. spectrum of this mixture in Me_2SO-d_6 is also shown in Fig. 1.

The spectral analysis was greatly facilitated by the availability of data on D-



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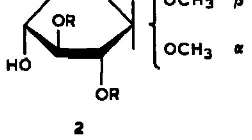

2

R = H or CH_3

TABLE I

CARBON-13 CHEMICAL SHIFTS[a] OF *O*-METHYL D-GLUCOSES (**1**) IN ACIDIFIED AQUEOUS SOLUTION

Anomer	*R-2*	*R-3*	*R-6*	*Label*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Me-2*	*Me-3*	*Me-6*
α	H	H	H	α0	92.11	71.53	72.83	69.78	71.47	60.71	—	—	—
β	H	H	H	β0	95.92	74.19	75.82	69.68	75.95	60.84	—	—	—
α	CH_3	H	H	α2	89.41	80.56	72.01	69.79	71.25	60.66	57.63	—	—
β	CH_3	H	H	β2	95.75	83.68	72.56	69.79	75.82	60.79	60.02	—	—
α	H	CH_3	H	α3	92.09	70.99	82.71	69.17	71.53	60.55	—	60.02	—
β	H	CH_3	H	β3	95.92	73.52	85.35	69.01	75.82	60.69	—	59.76	—
α	H	H	CH_3	α6	92.07	71.47	72.75	69.78	70.00	71.17	—	—	58.52
β	H	H	CH_3	β6	95.92	74.11	75.74	69.79	74.47	71.25	—	—	58.61
α	CH_3	CH_3	H	α23	89.34	80.09	81.91	69.17	71.34	60.55	57.50	59.87	—
β	CH_3	CH_3	H	β23	95.75	83.22	84.96	69.06	75.68	60.66	59.76	59.76	—
α	CH_3	H	CH_3	α26	89.39	80.49	71.94	69.79	69.89	71.10	57.63	—	58.52
β	CH_3	H	CH_3	β26	95.75	83.58	75.20	69.89	74.36	71.17	60.02	—	58.61
α	H	CH_3	CH_3	α36	92.06	70.92	82.60	69.29	70.07	71.07	—	59.97	58.52
β	H	CH_3	CH_3	β36	95.92	73.42	85.25	69.06	74.36	71.10	—	59.76	58.61
α	CH_3	CH_3	CH_3	α236	89.36	80.00	81.81	69.29	69.92	70.99	57.50	59.84	58.52
β	CH_3	CH_3	CH_3	β236	95.75	83.10	84.87	69.13	74.23	71.07	59.71	59.87	58.61

[a] Methanol served as the internal standard, with a shift of 49.00 p.p.m.

TABLE II

CARBON-13 CHEMICAL SHIFTS[a] OF *O*-METHYL DERIVATIVES OF METHYL D-GLUCOSIDES (2) IN Me_2SO-d_6 SOLUTION

Anomer	*R-2*	*R-3*	*R-6*	*Label*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Me-1*	*Me-2*	*Me-3*	*Me-6*
α	H	H	H	α0	101.32	73.61	74.98	71.96	74.22	62.57	56.03	—	—	—
β	H	H	H	β0	105.50	74.93	78.26	71.66	78.43	62.58	57.55	—	—	
α	CH_3	H	H	α2	98.30	82.80	74.02	71.96	74.02	62.53	55.85	59.17	—	—
β	CH_3	H	H	β2	105.14	85.03	77.51	71.81	78.28	62.53	57.63	61.38	—	—
α	H	CH_3	H	α3	101.30	73.23	85.27	71.11	74.28	62.49	55.94	—	61.60	—
β	H	CH_3	H	β3	105.43	74.62	88.22	70.96	78.30	62.49	57.69	—	61.56	—
α	H	H	CH_3	α6	101.29	73.46	74.93	71.94	72.55	73.59	55.75	—	—	60.00
β	H	H	CH_3	β6	105.40	74.87	78.15	71.64	76.99	73.52	57.53	—	—	60.08
α	CH_3	CH_3	H	α23	98.03	82.48	84.41	71.15	74.13	62.35	55.98	58.98	61.67	—
β	CH_3	CH_3	H	β23	105.06	84.64	87.45	71.10	78.15	62.35	57.69	61.18	61.63	—
α	CH_3	H	CH_3	α26	98.33	82.66	73.97	71.94	72.34	73.49	55.92	59.17	—	60.04
β	CH_3	H	CH_3	β26	105.02	84.91	77.40	71.79	76.82	73.39	57.61	61.38	—	60.14
α	H	CH_3	CH_3	α36	101.26	73.08	85.20	71.11	72.63	73.37	55.75	—	61.60	59.95
β	H	CH_3	CH_3	β36	105.31	74.52	88.09	70.95	76.86	73.27	57.57	—	61.56	60.16
α	CH_3	CH_3	CH_3	α236	98.06	82.33	84.33	71.15	72.47	73.23	55.87	58.98	61.63	60.02
β	CH_3	CH_3	CH_3	β236	104.94	84.52	87.33	71.10	76.70	73.20	57.66	61.18	61.60	60.12

[a] The central peak of the solvent resonance served as the internal standard, at 41.11 p.p.m.

TABLE III

MONOMER COMPOSITIONS OF *O*-METHYLCELLULOSES, AND CONFORMITY TO THEORETICAL MODELS

Quantity	*Sample A*				*Sample B*			
	Exptl.[a]	*Model I*	*Model II*	*Model III*	*Exptl.*[a]	*Model I*	*Model II*	*Model III*
s_0	9.9	7.5	9.1	9.2	5.4	3.5	4.5	4.6
s_2	17.5	17.4	15.8	15.8	11.8	12.1	11.1	11.1
s_3	1.8	4.0	2.4	2.4	2.3	3.3	2.3	2.3
s_6	14.0	12.1	14.7	14.7	9.9	8.2	10.6	10.7
s_{23}	9.2	9.3	11.0	10.9	10.9	11.2	12.1	12.0
s_{26}	23.8	28.1	25.5	25.5	25.2	28.1	25.9	25.9
s_{36}	4.5	6.5	3.9	3.9	5.4	7.6	5.3	5.4
s_{236}	19.4	15.1	17.6	17.6	29.5	26.1	28.3	28.0
σ[b]		2.6	1.3	1.3		2.0	0.8	0.8
d.s.	1.67				1.96			

[a] In mole% ±0.4. [b] Standard deviation between calculated and experimental values.

D-glucose[4] and the methyl D-glucosides[13] and literature data on the mono-*O*-methyl-D-glucoses[9] and the permethylated methyl D-glucosides[10]. Also available were data for 3-*O*-methyl-D-glucose, 2,6-di-*O*-methyl-D-glucose, 2,3,6-tri-*O*-methyl-D-glucose, and the corresponding methyl D-glucosides. Thus, for each mixture of 16 components, data on 8 of them were on hand. These, along with the literature data, were used in order to obtain estimates of the substituent effects on ^{13}C chemical shifts. The latter led to an initial, tentative identification of the spectral lines of the remaining 8 components. Detailed curve-fitting of the spectrum yielded the relative, integrated intensities of the individual lines, which were used in obtaining final assignments. The complete sets of chemical-shift data are summarized in Tables I and II. The mole fractions of the individual monosaccharides, *i.e.*, the monomer compositions, are given in Table III.

Some of the spectral bands are identified in Fig. 1. The spectrum of methanolyzed MC exhibits considerably better resolution than that of hydrolyzed MC; as discussed in the next section, this is due to the larger sustituent effects in the methyl D-glucoside series. The possibility that the solvent could be responsible for the better resolution was precluded after the spectrum of hydrolyzed MC had been recorded in Me_2SO-d_6. The result was that, for some spectral bands, the resolution actually deteriorated. The spectral band containing the resonances of substituted C-2 and C-3 is among the best resolved. Of the 16 components of the mixtures, 12 have resonances in this region. Only the signals of the anomers of unsubstituted, D-glucose and of 6-*O*-methyl-D-glucose are missing. Good resolution is also observed in the C-1 region of the spectrum of the methanolyzed sample. These two spectral regions are shown on expanded scales in Fig. 2, where the individual resonances are identified. The high quality of the spectra in terms of resolution and signal-to-noise ratio give confidence in the quantitative results for the mole fractions of the individual components in these mixtures.

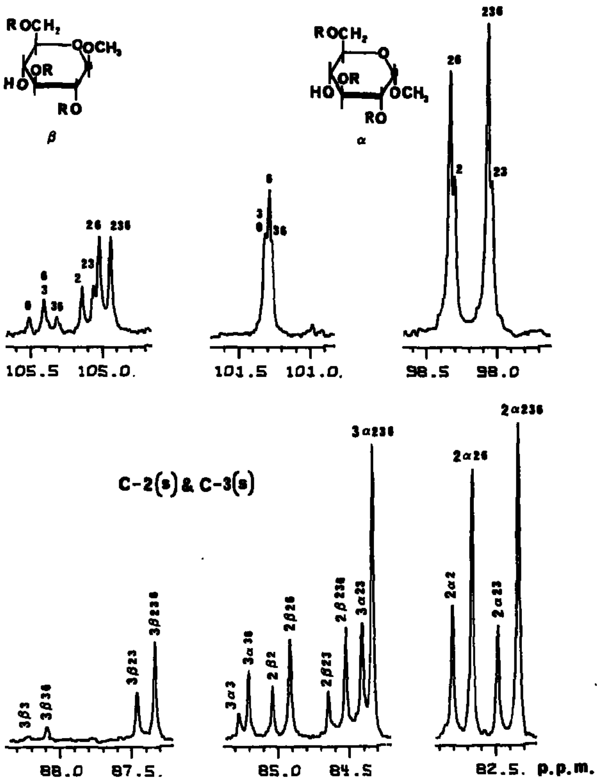

Fig. 2. The expanded spectral regions of C-1 and substituted carbon atoms 2 and 3 of methanolyzed *O*-methylcellulose.

DISCUSSION

Substituent effects on chemical shifts. — The availability of data obtained under identical experimental conditions, *i.e.*, free from possible complications due to differences in concentration and temperature, permits a meaningful discussion of substituent effects in ^{13}C chemical shifts. The results are summarized in Table IV. In general, the substituent effects were found to be additive to within ±0.04 p.p.m. However, some important exceptions to the additivity rule were observed. Thus, in the methyl D-glucoside series (see Table II), substitution at O-2 affects the magnitude of the effect of substitution at O-3 on the chemical shift of C-1. The following inequalities were observed.

$$\delta(1\alpha0) - \delta(1\alpha3) < \delta(1\alpha2) - \delta(1\alpha23) \qquad (26)$$

$$\delta(1\alpha6) - \delta(1\alpha36) < \delta(1\alpha26) - \delta(1\alpha236) \qquad (27)$$

TABLE IV

SUBSTITUENT EFFECTS[a] OF METHYLATION ON THE CARBON-13 CHEMICAL SHIFTS OF D-GLUCOSES AND METHYL GLUCOSIDES

Substitution	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
D-*Glucoses* (**1**)						
2α	−2.71	9.06	−0.80	0.01	−0.16 ±0.06	−0.05
2β	−0.17	9.58 ±0.11	−0.47 ±0.09	0.08	−0.13	−0.05
3α	−0.03	−0.51	9.88	−0.56	0.06	−0.12
3β	0.00	−0.58 ±0.11	9.60 ±0.10	−0.72	−0.13	−0.13
6α	−0.01	−0.07	−0.09	0.06	−1.42 ±0.06	10.46
6β	0.00	−0.10	−0.08	0.08	−1.46	10.41
Methyl D-*glucosides*(**2**)						
2α	−3.11 ±0.15	9.22	−0.91	−0.02	−0.18	−0.11
2β	−0.37	10.04	−0.76	0.15	−0.16	−0.10
3α	−0.15 ±0.12	−0.35	10.33	−0.82	0.10	−0.18
3β	−0.08	−0.36	9.94	−0.70	−0.13	−0.18
6α	0.00 ±0.03	−0.15	−0.06	−0.01	−1.67	10.94
6β	−0.12	−0.10	−0.12	−0.01	−1.45	10.86

[a] Average values, in p.p.m. ±0.04; where specified otherwise, median values are given.

This phenomenon is rather conspicuous in the spectral bands centered at 101.3 and 98.3 p.p.m. (see Fig. 2), and is responsible for the different resolution of the signals in these bands. Also seen in these bands is that substitution at O-3 affects the magnitude of the effect of substitution at O-2. This result can be obtained algebraically by rearranging Eqs. *26* and *27*. Thus, *e.g.*, from Eq. *26* is obtained

$$\delta(1\alpha0) - \delta(1\alpha2) < \delta(1\alpha3) - \delta(1\alpha23) \qquad (28)$$

These findings suggest that the ***nonadditivity of substituent effects results from an interaction between the substituents.***

The results for the D-glucose series (see Tables IV and I) indicate relatively large (>±0.04 p.p.m.) deviations from additivity for C-2β and C-3β, with an interaction between the substituents at O-2 and O-3, and for C-5α, with an interaction between the substituents and O-2 and O-6; and, of course, the most prominent interaction between substituents involves the substituent at O-1, resulting in the different resolution in the spectra of hydrolyzed and methanolyzed MC. In general, the substituent effects in the methyl D-glucoside series are larger than in the D-glucose series (see Table IV).

Monomer composition and models for its description. — The conformity of the data on the monomer composition to theoretical models was tested by comparing the experimental results with the expectation values from each of the three models and calculating the standard deviation. The results of these calculations are given in Table III. The difference between the models becomes

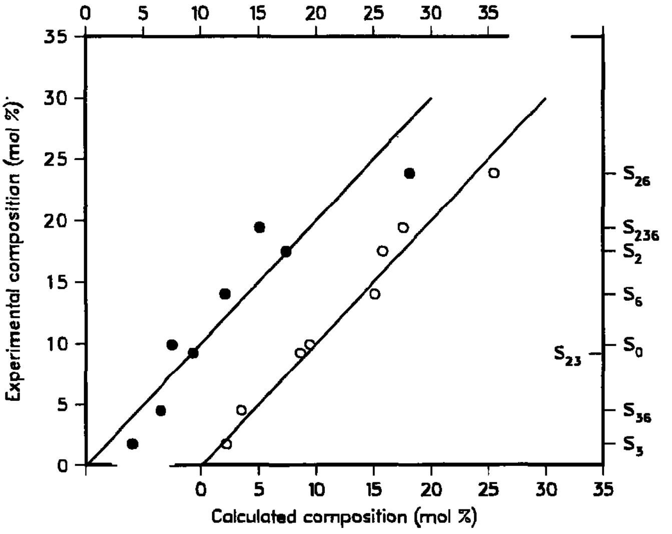

Fig. 3. Experimental *versus* calculated values of the monomer mole fractions of hydrolyzed *O*-methylcellulose (Sample A): Model I, filled circles; Model II, open circles (with abscissa displaced by 10 units for clarity). The lines describe ideal behavior.

quite evident in plots of experimental *versus* calculated values (see Figures 3 and 4). Inspection of these plots for Model I indicates considerable scatter and non-random distributions of points about the line describing ideal behavior. Both the standard deviation and the scatter diminish substantially with the results from

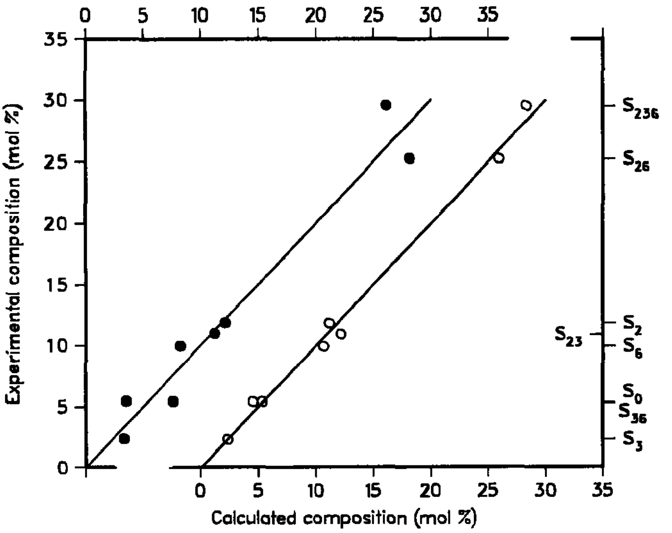

Fig. 4. Experimental *versus* calculated values of the monomer mole fractions of methanolyzed *O*-methylcellulose (Sample B): Model I, filled circles; Model II, open circles (with abscissa displaced by 10 units for clarity). The lines describe ideal behavior.

TABLE V

RELATIVE FIRST-ORDER RATE CONSTANTS OF METHYLATION OF CELLULOSE

Quantity	*Sample A*		*Sample B*	
	Model I	*Model II*	*Model I*	*Model II*
k_2	1.25	1.25	1.24	1.24
k_3	0.45	0.22	0.55	0.34
k_3'	—	0.85	—	0.78
k_6	[1.00]	[1.00]	[1.00]	[1.00]

Model II. No further improvement is obtained with Model III. A summary of the relative rate-constants obtained with Models I and II is given in Table V. The results for the two samples are rather similar. The differences in the values of k_2 and k_3' ($k_6 = 1.00$ is assumed for both samples) are within the experimental errors. The larger difference for k_3 is indicative of differences in some of the process conditions used in the production of these materials.

Although the values of the realtive rate-constants obtained in this work differ from those reported by Croon[7,12] for laboratory preparations of MC, the main conclusion is the same. In the reaction leading to the production of MC, the reactivity of OH-3 is substantially modified by substitution at O-2. Among the possible reasons[7,14] for this phenomenon, inductive effects and the involvement of OH-3 in an intramolecular hydrogen-bond are probably the key factors.

EXPERIMENTAL

The samples of MC and 3-*O*-methyl-D-glucose were commercially available products. Cyclodextrin derivatives (obtained from Aldrich Chemical Co.) were used in the preparation of 2,6-di- and 2,3,6-tri-*O*-methyl-D-glucose and the corresponding methyl D-glucosides. Hydrolysis was achieved by using perchloric acid in a procedure previously described for CMC[4]. For the methanolysis, the material (1 g) was dissolved in dry methanolic HCl (20 mL; acid content >M). The treatment was conducted for 1 week at 60°, and the resulting solution of methyl glucoside derivatives was evaporated in a rotary evaporator at 3.3 kPa and 60° (water bath). The resulting syrup was mixed with Me_2SO-d_6 (5 mL) and the suspension filtered into a n.m.r. tube.

^{13}C-N.m.r. spectra were recorded at 90.56 MHz with a Nicolet 360 WB spectrometer operated at 26 ±1° in the Fourier-transform mode. Low-power proton-decoupling was achieved by using the MLEV-64 pulse sequence[15]. Other details were similar to those previously described[4].

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