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ANALYSIS OF THE CARBON-13 N.M.R. SPECTRUM OF METHANOLYZED *O*-ETHYLCELLULOSE: MONOMER COMPOSITION AND MODELS FOR ITS DESCRIPTION

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ABSTRACT

The carbon-13 n.m.r. spectrum of methanolyzed *O*-ethylcellulose was assigned in detail. The monomer composition was obtained from the relative peak-areas. The results indicated that the reactivity of hydroxyl-3 increases upon ethylation of hydroxyl-2. The relative rate-constants of the hydroxyl groups in the ethylation reaction are $k_2:k_3:k_3':k_6 = 0.94:0.22:0.98:1.00$.

INTRODUCTION

In one process of preparing *O*-ethylcellulose (EC), the hydroxyl groups on C-2, -3, and -6 of the D-glucosyl residues of cellulose react with ethyl chloride to give ethyl ethers at these positions. Because the reaction is usually not carried to completion, only part of the hydroxyl groups are substituted. As a result, a copolymer of eight monomers is obtained. The analysis of such materials in terms of monomer composition is usually a difficult task.

Recently, complete and accurate spectral assignments of the carbon-13 n.m.r. spectra of hydrolyzed and methanolyzed samples of *O*-methylcellulose were obtained[1]. It was found that the monomer composition of *O*-methylcellulose can be described by a statistical, kinetic model which takes account of the possibility that the reactivity of hydroxyl-3 may depend on the state of substitution at O-2. The results indicated that the relative rate constant of methylation of hydroxyl-3 increases threefold upon methylation of hydroxyl-2. In light of these findings, an examination was undertaken of the spectrum of a methanolyzed EC sample. By using the spectral data on the methylated methyl D-glucosides[1] as a guide, a complete and accurate assignment of the carbon-13 n.m.r. spectrum of methanolyzed EC was achieved. This paper summarizes the spectral data and provides an interpretation of the monomer composition in terms of kinetic models and relative rate constants.

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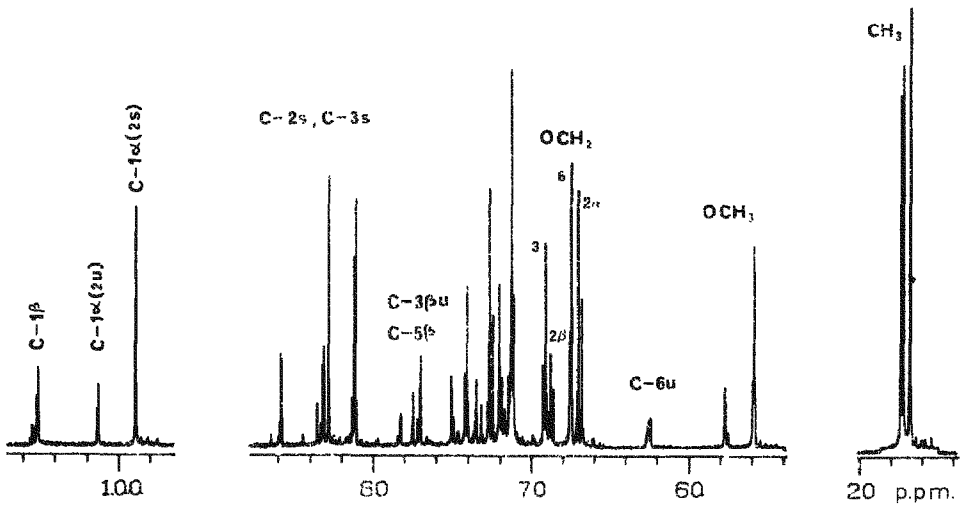


Fig. 1. Carbon-13 n.m.r. spectrum of methanolyzed *O*-ethylcellulose. Some of the assignments are indicated (s denotes substituted; u, unsubstituted).

RESULTS AND DISCUSSION

The EC sample investigated in this work was a laboratory preparation having an average degree of substitution of 2.10.

Carbon-13 n.m.r. spectrum. — The spectrum of the methanolyzed sample is shown in Fig. 1. As anticipated, this spectrum exhibits many similarities to that of methanolyzed *O*-methylcellulose[1]. The spectral assignments were obtained by comparison with the latter. Some of the better resolved and information-rich portions

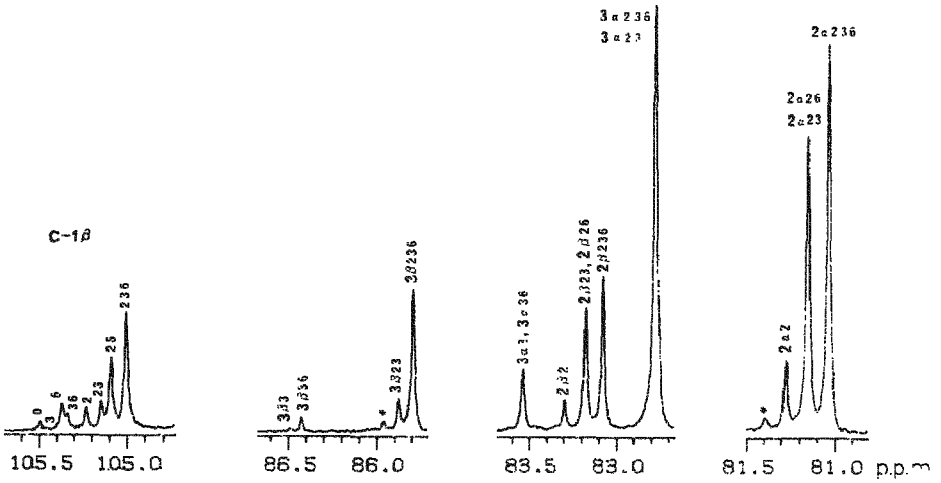
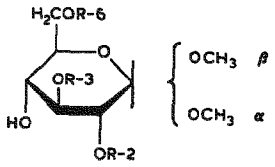


Fig. 2. Expanded spectral regions of carbon-1 of the β anomers, and substituted carbon atoms 2 and 3, with assignments. (Asterisks denote impurities.)

of the spectrum are shown on an expanded scale in Fig. 2, where the assignments of individual peaks are given. A number of minor peaks are probably due to methyl cellobioside impurities that result from incomplete methanolysis.

The carbon-13 chemical shifts of the ethylated methyl D-glucosides of the general formula



R = CH_2CH_3 or H

are summarized in Table I. Table II gives the effect of ethylation on the chemical shifts. The substituent effects are usually additive to within ±0.04 p.p.m. Larger deviations, extending up to ±0.11 p.p.m., are observed in a few cases (see Table II). A similar phenomenon has been observed for the effects of methylation, and was attributed to interactions between the substituents[1].

The substituent effects of ethylation are, in general, smaller than those of methylation. Thus, *e.g.*, ethylation at O-2 leads to a downfield shift of the C-2 signal of 7.80 and 8.40 p.p.m. for the α and β anomers, respectively. The respective values for methylation are 9.22 and 10.04 p.p.m. The difference of ~1.5 p.p.m. is due to the well known "γ-effect" on carbon-13 chemical shifts[2].

Monomer composition, and models for its description. — The mole fraction s_i (where i indicates the position of substitution) for each of the individual monosaccharides was obtained from the integrated intensities of the individual peaks. The results are summarized in Table III.

Statistical, kinetic models for the description of the arrangement of substituents (monomer composition) in cellulose ethers have been presented by Spurlin[3]. For the present discussion, there will be considered the model that involves the following assumptions: (*a*) all D-glucosyl residues are equally accessible for reaction; (*b*) substitution within a given D-glucosyl unit does not affect the reactivity of the remaining hydroxyl groups, with the exception that the reactivity of OH-3 depends on the state of substitution at O-2; (*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; and (*d*) the effect of end groups is negligible. According to this general model, four relative rate constants must be considered: k_2, k_3, k_3', and k_6, where k_3' is the relative rate constant of OH-3 when O-2 is ethylated. For convenience, we define the probability functions

$$p_i = e^{-Bk_i} \qquad (1)$$

TABLE I

CARBON-13 CHEMICAL SHIFTS[a] OF *O*-ETHYL DERIVATIVES OF METHYL D-GLUCOSIDES 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*	CH_3O	CH_2O-2	CH_2O-3	CH_2O-6
α	H	H	H	α0	101.23	73.56	74.98	71.92	74.17	62.56	55.83	—	—	—
β	H	H	H	β0	105.49	74.95	78.23	71.62	78.39	62.66	57.51	—	—	—
α	C_2H_5	H	H	α2	98.94	81.27	74.03	72.00	73.96	62.50	56.71	66.75[b]	—	—
β	C_2H_5	H	H	β2	105.23	83.29	77.49	71.81	78.23	62.50	57.68	68.54[c]	—	—
α	H	C_2H_5	H	α3	101.31	73.23	83.53	71.12	74.29	62.43	55.89		68.75[d]	—
β	H	C_2H_5	H	β3	105.46	74.69	86.49	71.12	78.34	62.50	57.61		68.94[d]	—
α	H	H	C_2H_5	α6	101.22	73.46	74.98	71.98	72.66	71.29	55.89	—	—	67.40[e]
β	H	H	C_2H_5	β6	105.36	74.85	78.19	71.67	77.15	71.41	57.43	—	—	67.51[e]
α	C_2H_5	C_2H_5	H	α23	98.88	81.15	82.77	71.22	74.17	62.36	55.74	66.97[b]	69.00[d]	—
β	C_2H_5	C_2H_5	H	β23	105.14	83.17	85.87	71.25	78.19	62.46	57.71	68.71[c]	69.17[d]	—
α	C_2H_5	H	C_2H_5	α26	98.94	81.15	74.03	72.02	72.45	71.25	55.78	66.75[b]	—	67.40[e]
β	C_2H_5	H	C_2H_5	β26	105.09	83.17	77.43	71.84	76.98	71.34	57.61	68.54[c]	—	67.51[e]
α	H	C_2H_5	C_2H_5	α36	101.31	73.14	83.53	71.18	72.89	71.18	55.86	—	68.83[d]	67.40[e]
β	H	C_2H_5	C_2H_5	β36	105.33	74.57	86.42	71.18	77.08	71.22	57.48	—	68.94[d]	67.51[e]
α	C_2H_5	C_2H_5	C_2H_5	α236	98.88	81.03	82.77	71.25	72.66	71.12	55.78	66.97[b]	69.06[d]	67.40[e]
β	C_2H_5	C_2H_5	C_2H_5	β236	105.00	83.07	85.79	71.29	76.93	71.18	57.64	68.71[c]	69.24[d]	67.51[e]

[a]The central peak of the solvent resonance served as an internal standard at 41.11 p.p.m. [b]Methyl at 17.14 p.p.m. [c]Methyl at 17.19 p.p.m. [d]Methyl at 17.32 p.p.m. [e]Methyl at 16.73 p.p.m.

TABLE II

EFFECTS OF ETHYLATION ON CARBON-13 CHEMICAL SHIFTS[a] OF METHYL D-GLUCOSIDES

Substitution	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
2α	−2.36 ±0.07	7.80 ±0.11	−0.85 ±0.09	0.07	−0.17	−0.06
2β	−0.30	8.40 ±0.08	−0.69 ±0.07	0.15	−0.16	−0.05
3α	0.01 ±0.07	−0.23 ±0.11	8.64 ±0.10	−0.79	0.17	−0.13
3β	−0.06	−0.18 ±0.08	8.31 ±0.07	−0.53	−0.05	−0.16
6α	0.00	−0.11	0.00	0.04	−1.51	8.75
6β	−0.14	−0.10	−0.06	0.04	−1.25	8.73

[a]In p.p.m. ±0.04, except where noted otherwise.

where k_i is a first-order rate constant and B is a factor with the dimension of time. The following set of equations describes the mole fractions of the individual monomers

$$s_0 = p_2 p_3 p_6 \tag{2}$$
$$s_2 = p_6 R \tag{3}$$
$$s_3 = x_3 p_2 p_6 \tag{4}$$
$$s_6 = x_6 p_2 p_3 \tag{5}$$
$$s_{23} = p_6 (x_2 - R) \tag{6}$$
$$s_{26} = x_6 R \tag{7}$$
$$s_{36} = x_3 x_6 p_2 \tag{8}$$
$$s_{236} = x_6 (x_2 - R) \tag{9}$$

TABLE III

EXPERIMENTAL AND CALCULATED MONOMER MOLE PERCENTAGES AND RELATIVE RATE CONSTANTS

Parameter	*Exptl.*	*M-I*[a]	*M-II*[b]
s_0	4.4	2.3	3.6
s_2	7.1	7.3	6.0
s_3	0.9	2.7	1.4
s_6	12.3	8.3	13.1
s_{23}	8.9	8.9	10.2
s_{26}	21.3	27.2	22.4
s_{36}	5.9	10.2	5.3
s_{236}	39.2	33.1	37.9
d.s.	2.10		
σ[c]		3.8	1.0
k_2/k_6		0.94	0.94
k_3/k_6		0.52	0.22
k_3'/k_6		—	0.98

[a]Calculated according to Model I. [b]Calculated according to Model II. [c]Standard deviation between experimental and calculated values.

where

$$x_i = 1 - p_i \tag{10}$$

and

$$R = k_2\,(p_3' - p_2\,p_3)/(k_2 + k_3 - k_3'). \tag{11}$$

Detailed analyses have shown[4] that, for *O*-(carboxymethyl)cellulose, there is no correlation between the reactivities of the hydroxyl groups on C-2 and C-3. On the other hand, for an *O*-methylcellulose, such a correlation has been established[1]. Therefore, it is instructive to break the above model into two models: Model I, where $k_3' = k_3$ and $R = x_2\,p_3$, and Model II, where $k_3' \neq k_3$. With a set of experimental data on the monomer composition (values of s_i), the conformity to these models can be tested in the following fashion.

Model I. Positional degrees of substitution are calculated as

$$x_2 = s_2 + s_{23} + s_{26} + s_{236} \tag{12}$$

$$x_3 = s_3 + s_{23} + s_{36} + s_{236} \tag{13}$$

$$x_6 = s_6 + s_{26} + s_{36} + s_{236} \tag{14}$$

$$\text{d.s.} = x_2 + x_3 + x_6 \tag{15}$$

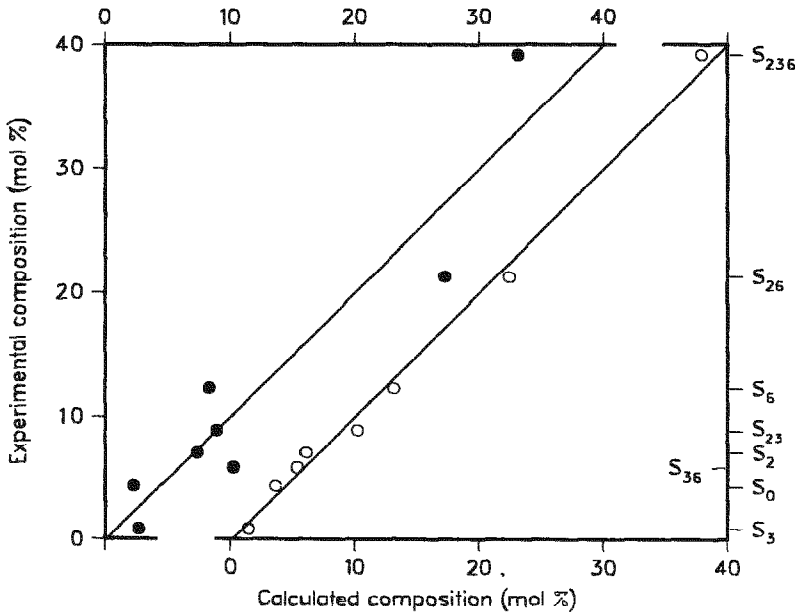


Fig. 3. Experimental *versus* calculated values of the monomer mole percentages: Model I, filled circles; Model II, open circles. The lines describe ideal behavior.

Values of p_i are calculated with Eq. *10*. Expectation values of s_i are calculated with the appropriately simplified versions of Eqs. *2–9*.

Model II. The positional degrees of substitution x_2 and x_6 are calculated with Eqs. *12* and *14*, respectively. The other necessary quantitites are obtained as

$$p_3 = (1 - x_2 + s_0 + s_6 - s_3 - s_{36})/2(1 - x_2) \quad (16)$$

$$R = s_2 + s_{26} \quad (17)$$

The results of the calculations according to the two models, along with the standard deviation from the experimental values are given in Table III. These results show that the conformity to Model II is much the better of the two. This observation is graphically demonstrated by the plot given in Fig. 3. Similar behavior has been observed with *O*-methylcellulose[1].

In crystalline cellulose, OH-3 is engaged in an intramolecular hydrogen-bond. As a result, its reactivity is much hindered relative to the hydroxyl groups on C-2 and C-6. It has been found that, for simple monosaccharides, the difference between the reactivities of the different hydroxyl groups is minimal[5]. Thus, structural changes in the cellulose molecule that are induced by ethylation are likely to lead to disruption of intramolecular hydrogen-bonds and to enhancement of the reactivity of hydroxyl-3.

The present results on the relative rate constants are in agreement with those of Mahoney and Purves[6], who hydrolyzed a commercial sample and then traced the positions of vicinal diols by oxidation. On the other hand, by fractionating the hydrolyzate of a laboratory preparation on a carbon column, Croon and Flamm[7] found $k_2:k_3:k_6 = 4.5:1.0:2.0$. The reasons for this discrepancy are unknown.

EXPERIMENTAL

The sample of *O*-ethylcellulose was a gift from Dr. P. E. Barnum. Other experimental details were similar to those previously described for *O*-methylcellulose[1]. The carbon-13 n.m.r. spectrum was recorded at 90.56 MHz for a solution of the methanolyzed sample in Me_2SO-d_6.

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