

# Preparation and Structural Consideration of Nitrogen-Containing Derivatives Obtained from Dialdehyde Celluloses

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## SYNOPSIS

Nitrogen-containing derivatives obtained from dialdehyde celluloses were prepared under different pH conditions. On the basis of the results from an analytical data and IR absorption spectra of the products, the structure and characterization of nitrogen-containing products are discussed and also evaluated concerning a hemialdal seven-membered cyclic structure proposed by Barry *et al.* (*J. Chem. Soc.*, **1953**, 3631).

## INTRODUCTION

Periodate oxidation of cellulose gives a ring-opened product containing two aldehyde groups formed by oxidative scission at the C-2 and C-3 of the anhydro D-glucopyranose residues in the cellulose molecule.<sup>1,2</sup> The periodate oxidation is generally characterized by its selective cleavage of the carbon-carbon bond between vicinal hydroxyl groups. The oxycellulose is referred to dialdehyde cellulose, and can be regarded as a kind of intermediate containing reactive aldehyde groups. However, the dialdehyde cellulose is extremely sensitive to alkali and acid owing to the formation of the ring-opened structure of the anhydro glucose units, giving degradation products such as 2,4-dihydroxybutanoic acid from alkali degradation<sup>2</sup> and D-erythrose from acid degradation.<sup>1,3</sup> The structure of dialdehyde cellulose, as shown in Figure 1, has been suggested to include the hydrated form  $[-CH(OH)_2]$ , the 2,3-hemialdal form  $[-CH(OH)-O-CH(OH)-]$ , the 2,6- or 3,6-hemiacetal forms  $[-CH(OH)-O-CH_2-]$ , as well as the reactive free aldehyde form.<sup>2,4</sup> The former three types correspond to addition of one molecule of water per each aldehyde group, addition of one molecule of water per two aldehyde groups, and

rearrangement between an aldehyde group and one of the remaining alcohol groups without addition of water. All forms act as free aldehydes under appropriate conditions. According to a kinetic study,<sup>2</sup> free or hydrated aldehyde groups react about 300 times faster than hemialdal groups, and hemiacetal groups come in intermediate between both forms. The reaction rate of hemialdal groups is five times higher than that of the reducing end groups in hydrocellulose.<sup>2</sup> The dialdehyde cellulose may be useful as an intermediate for various derivatives from cellulose. In particular, dialdehyde cellulose can give various nitrogen-containing derivatives in good yield by reaction at ambient temperature in aqueous medium. The aldehyde groups in the anhydro glucose unit would be theoretically expected to give condensation products by the reaction with two molar reagents per anhydro glucose unit, as seen in the structure of (1) or (2)-1 shown in P-5 and P-7, because periodate oxidized products contain two free aldehyde groups in the anhydro glucose unit. However, Barry *et al.*<sup>5</sup> indicated previously that periodate oxidized polysaccharides gave condensation products containing only one molar reagent per anhydro monosaccharide unit, suggesting a possible seven-membered cyclic structure formed by a hemialdal linkage of (2)-3 or (3)-1 shown in P-7.

The nucleophilic reaction for addition-condensation between a carbonyl group and a basic amine or hydrazide reagent, as shown in Figure 2, depends

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for cellulose as proposed by Turbak et al.<sup>7</sup> Cellulose solid gel regenerated from a mixture of methanol and distilled water (1 : 1, v/v) was subjected to periodate oxidation in 0.1 M acetate buffer solution (pH 4.5, 500 mL) containing sodium metaperiodate (5.5 g) without drying as described previously. The final product was oxidized for 72 h. The final degree of oxidation was likewise determined according to the method<sup>6</sup> described previously. The value was 76.0%.

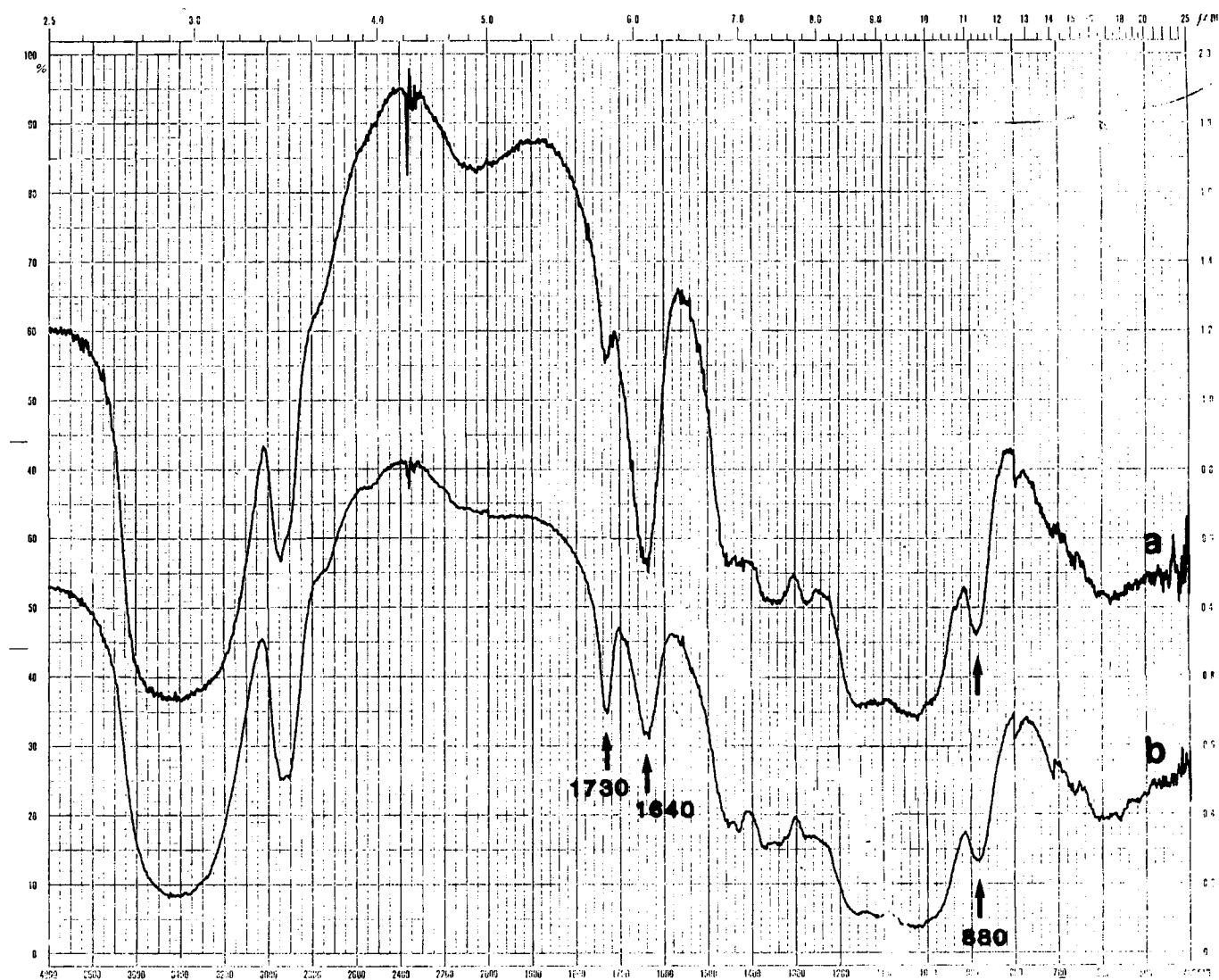
### Preparation of Dioximes from Dialdehyde Celluloses

Hydroxylamine hydrochloride (3.3 g) was added dropwise to an aqueous suspension of dialdehyde

cellulose in 0.1M acetate buffer solution. The reaction mixture was adjusted with sodium carbonate to keep the fixed pH value (pH 5.5) and allowed to react for 24 h. The reaction product was recovered through filtration as a pale brownish powder by the same procedure described above (P-1, yield: 3.66 g). The filtrates were concentrated to 50 mL volume after dialysis with cellulose tubing for desalting, and recovered as a powder by freeze-drying (P-2, yield: 0.65 g).

### Reduction of Dioximes

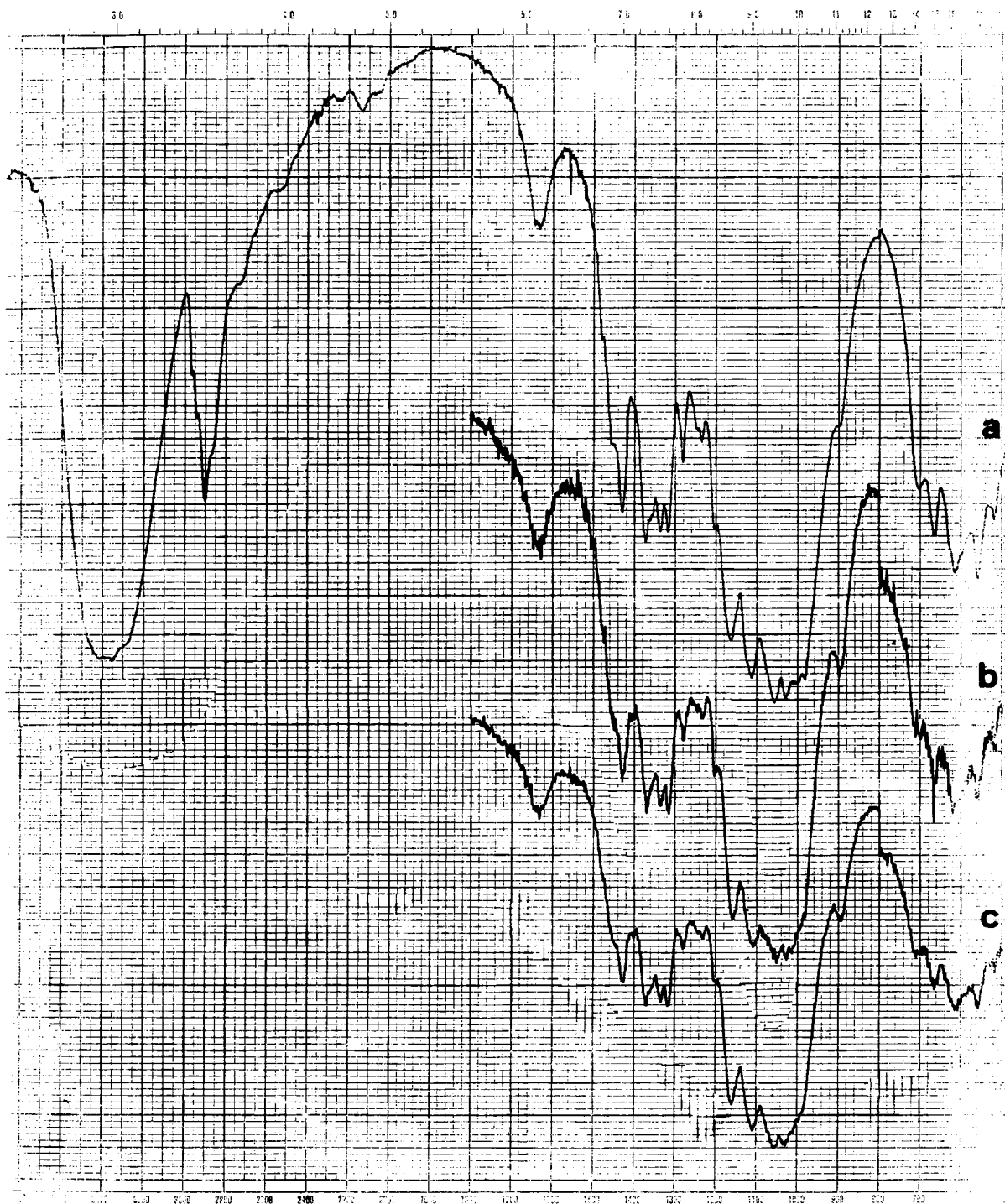
An aqueous suspension of dioxime (P-1, 1.5 g) in M/20 borate buffer solution (pH 9.5, 150 mL) was



**Figure 3** IR spectra of dialdehyde cellulose treated by heating: (a) dialdehyde cellulose obtained by usual drying; (b) dialdehyde cellulose treated by heating in a drying oven of 100°C, 24 h.

reduced with sodium borohydride (7 g) with stirring at room temperature. The reduction product was dissolved completely to give a clear solution. After decomposition of the extra reductant with acetic

acid, the solution was dialyzed against distilled water with cellulose tubing. The dialyzate solution was concentrated to 50 mL volume and freeze-dried (P-3, yield: 0.83 g).



**Figure 4** IR spectra of the products recovered after reaction with dialdehyde cellulose and hydroxylamine at the pH values of 3.0 and 4.0: (a) commercial Whatman crystalline cellulose powder CF-11; (b) product recovered at pH 3.0; (c) product recovered at pH 4.0.

### Treatment of Dioximes with Acetic Anhydride

Dry dioxime (P-1, 1.04 g) was mixed with anhydrous sodium acetate (2.5 g) and acetic anhydride (60 mL), and heated at 120°C for 1 h with stirring. The product was poured into ice water (300 mL) to give an oily material, which was precipitated by the addition of ethanol. The precipitate was collected by centrifugation and gave a pale brownish powder after washing with methanol and drying in vacuum (P-4, yield: 0.83 g, recovery 71.6%).

### Infrared Spectrometry

IR spectra of various samples prepared were measured in a KBr disk with an IR spectrometer of IR-810 type manufactured by Japan Spectroscopic Co. Ltd.

### Elemental Analyses

The elemental analyses of nitrogen-containing products were made by request to a center for elemental analysis at the Faculty of Pharmaceutical Science in our University.

## RESULTS AND DISCUSSION

### Changes of Dialdehyde Cellulose by Heating

As shown in Figure 3, dialdehyde cellulose prepared by usual method has no absorption of carbonyl group based on aldehyde group in IR spectrum. However, by heating treatment at 100°C for 24 h, characteristic absorption of masked carbonyl group was clearly appeared in the region of 1730  $\text{cm}^{-1}$  with decrease of absorption at near 1640  $\text{cm}^{-1}$  based on adsorbed water. The finding suggests that dialdehyde cellulose involves the structure formed by addition of water molecule.

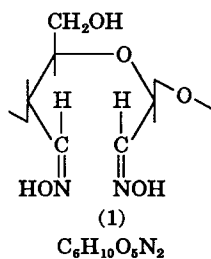
### Nitrogen-Containing Condensation Products from Dialdehyde Celluloses

The condensation product prepared from dialdehyde cellulose and hydroxylamine in a buffer solution adjusted to various pH values was most susceptible to changes of pH values. In the region of pH 3–4, dialdehyde cellulose was decomposed completely and the reaction medium turned to a yellow-brown product. A small amount of product recovered after

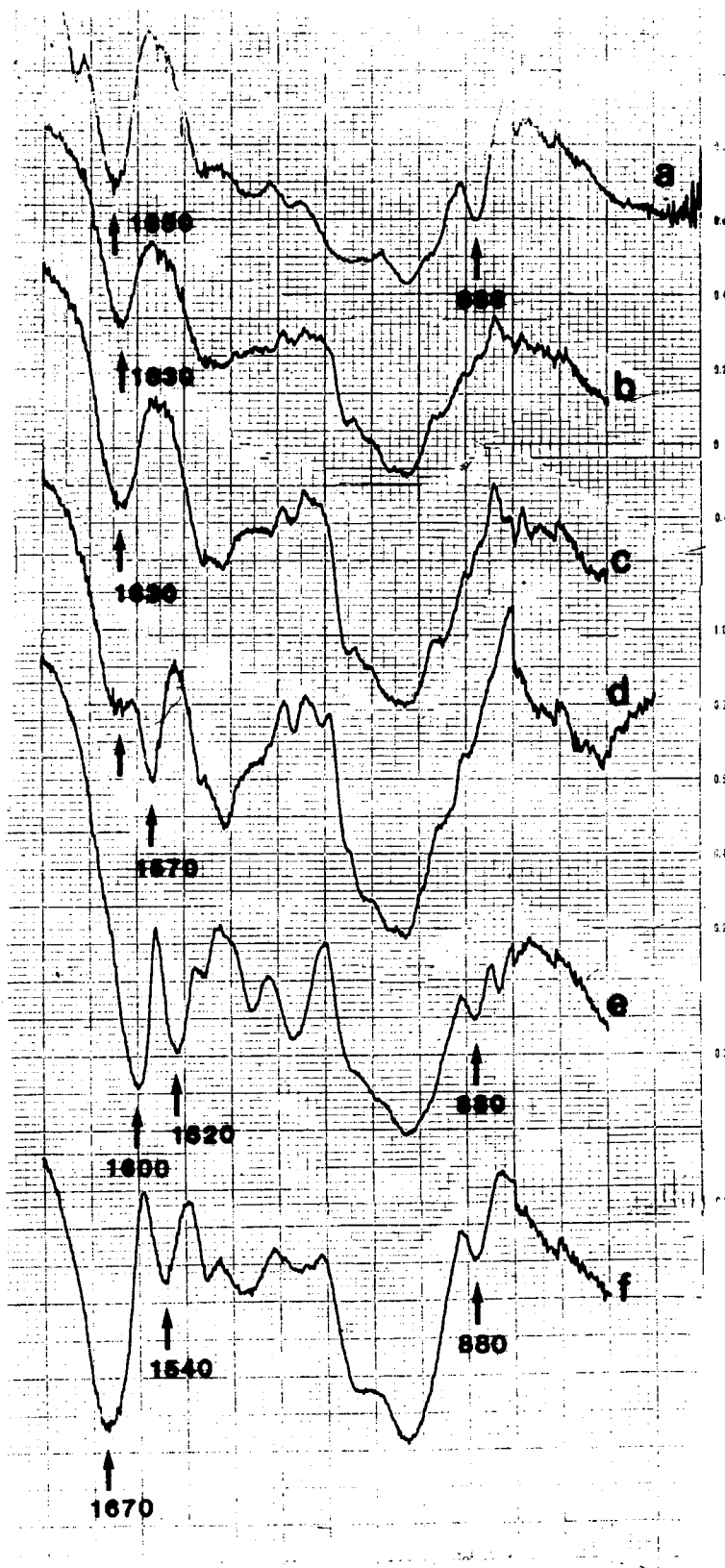
**Table I** Condensation Products of Dialdehyde Cellulose (DAC) and Hydroxylamine at Various pH Values

Sample	Reaction pH	Actual Yield (g)	Yield <sup>a</sup> (%)	Found		
				C (%)	H (%)	N (%)
I-30	3.0	0.059	5.2			
I-40	4.0	0.052	4.6			
I-50	5.0	0.996	87.3	38.19	5.69	11.16
I-55	5.5	1.044	91.5	37.77	5.77	12.29
I-60	6.0	1.029	90.2	38.29	5.82	11.59
I-70	7.0	0.659	57.8	37.69	5.63	12.61
I-80	8.0	0.505	44.3	38.28	5.54	12.39

<sup>a</sup> Yield (%) = actual yield (g)/theoretical yield (g) × 100. Note: Sample DAC used, 1.00 g (Oxidation ratio: 75.3%). Reaction temp: 20–25°C; reaction time: 24 h. These samples used were prepared at the corresponding reaction pH conditions. For example, I-30 means that the sample was prepared at the reaction pH of 3.0.



Theoretical yield: 1.141 g  
Calcd: C(%): 39.32  
H(%): 5.46  
N(%): 11.52

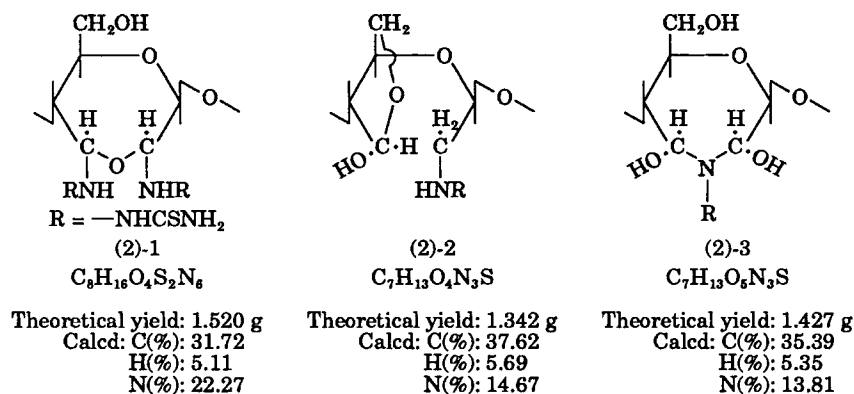


**Figure 5** IR spectra of nitrogen-containing derivatives derived from dialdehyde cellulose (DAC): (a) original DAC; (b) dioxime (P-1); (c) dioxime (P-2); (d) reduction product of dioxime (P-3); (e) condensation product of DAC and thiosemicarbazide; (f) condensation product of DAC and adipic acid hydrazide.

**Table II Condensation Products of Dialdehyde Cellulose and Thiosemicarbazide at Various pH Values**

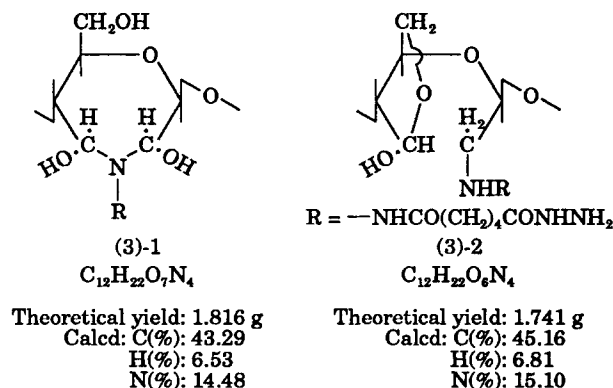
Sample	Reaction pH	Actual Yield (g)	Yield <sup>a</sup> (%)	Found		
				C (%)	H (%)	N (%)
II-30	3.0	1.419	99.4	32.94	5.25	19.24
II-40	4.0	1.411	98.9	32.73	5.24	19.37
II-50	5.0	1.338	93.8	33.45	5.35	17.48
II-55	5.5	1.331	93.3	33.89	5.37	16.05
II-60	6.0	1.350	94.6	33.82	5.70	15.68
II-70	7.0	1.369	95.9	33.37	5.24	14.94
II-80	8.0	1.348	94.5	33.30	5.38	15.00

<sup>a</sup> See Table I. Note: Sample DAC used, 1.00 g (Oxidation ratio: 75.3%). Reaction temp: 20–25°C; reaction: 36 h. See Table I on these samples used. II-30 means that the sample was prepared at the reaction pH of 3.0.


**Table III Condensation Products of Dialdehyde Cellulose and Adipic Acid Hydrazide at Various pH Values**

Sample	Reaction pH	Actual Yield (g)	Yield <sup>a</sup> (%)	Found		
				C (%)	H (%)	N (%)
III-30	3.0	1.360	78.6	43.52	6.32	10.89
III-50	5.0	1.453	83.9	44.44	6.51	12.68
III-55	5.5	1.457	84.2	44.58	6.54	12.45
III-60	6.0	1.451	83.8	44.13	6.61	12.08
III-80	8.0	1.404	81.1	39.54	6.28	10.67

<sup>a</sup> See Table I. Note: Sample DAC used 1.00 g (Oxidation ratio: 75.3%). Reaction temp: 20–25°C; reaction time: 30 h. See Table I on these samples used. III-30 means that the sample was prepared at the reaction pH of 3.0.



reaction at these pH values was identified as the original crystalline cellulose of no oxidation fragment from comparison with IR spectra shown in Figure 4. As shown in Table I, the condensation product prepared at the pH value of 5.5 gave the highest yield and the highest nitrogen content. With increase of reaction pH values, the recovered yields of the products decreased. Therefore, the pH value for preparation of dioxime is expected to be in the pH range of 5.0–6.0. By considering from nitrogen contents found in the products, dialdehyde cellulose reacts with two molecular hydroxylamine to give a dioxime as shown in the structure of (1). The conclusion can be derived from IR spectra of Figure 5. In Figure 5, an absorption based on the formation of oxime,  $\text{>C=N-}$ , is revealed at near  $1630\text{ cm}^{-1}$ ,

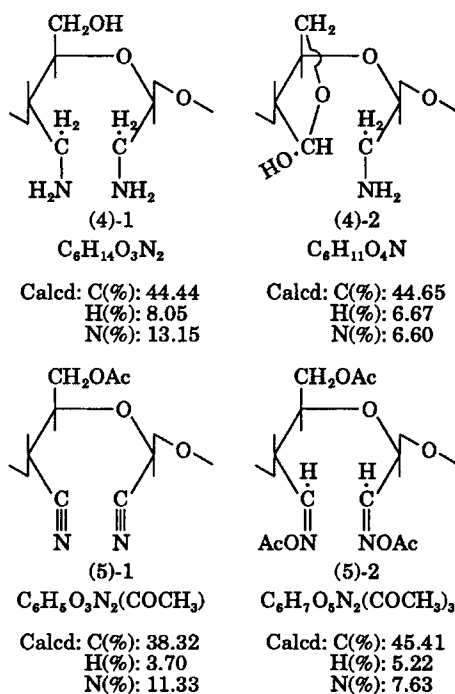
while an absorption at near  $880\text{ cm}^{-1}$ , which is observed in the IR spectrum (a) of dialdehyde cellulose, is not apparent as shown in the spectra (b) and (c) of dioxime. This finding leads to the conclusion that the dioxime structure as shown in (1) is most likely to be formed under conditions described above, because an absorption at near  $900\text{ cm}^{-1}$  based on the formation of a cyclic hemiacetal linkage<sup>1,8</sup> is not observed, and so dioxime has no intramolecular ring structure.

The elemental analyses and yields of condensation products prepared from dialdehyde cellulose and thiosemicarbazide at different pH ranges are given in Table II. In addition, the possible structures of the product in this case are presented with the theoretical elemental compositions. From the analytical result of only nitrogen contents introduced in the

**Table IV Analytical Data of Nitrogen-Containing Products Prepared from Dialdehyde Cellulose (DAC)**

Procedure	Yield <sup>a</sup> (%)	Found		
		C (%)	H (%)	N (%)
P-1 DAC + NH <sub>2</sub> OH	76.3	38.60	6.09	8.75
P-2		37.37	5.54	10.25
P-3 Reduction of P-1 with NaBH <sub>4</sub>	55.0	38.48	6.14	4.74
P-4 Treatment of P-1 with (CH <sub>3</sub> CO) <sub>2</sub> O 120°C, 1 h	71.6	45.53	5.21	5.38
		46.71	5.34	3.42

<sup>a</sup> See Table I.



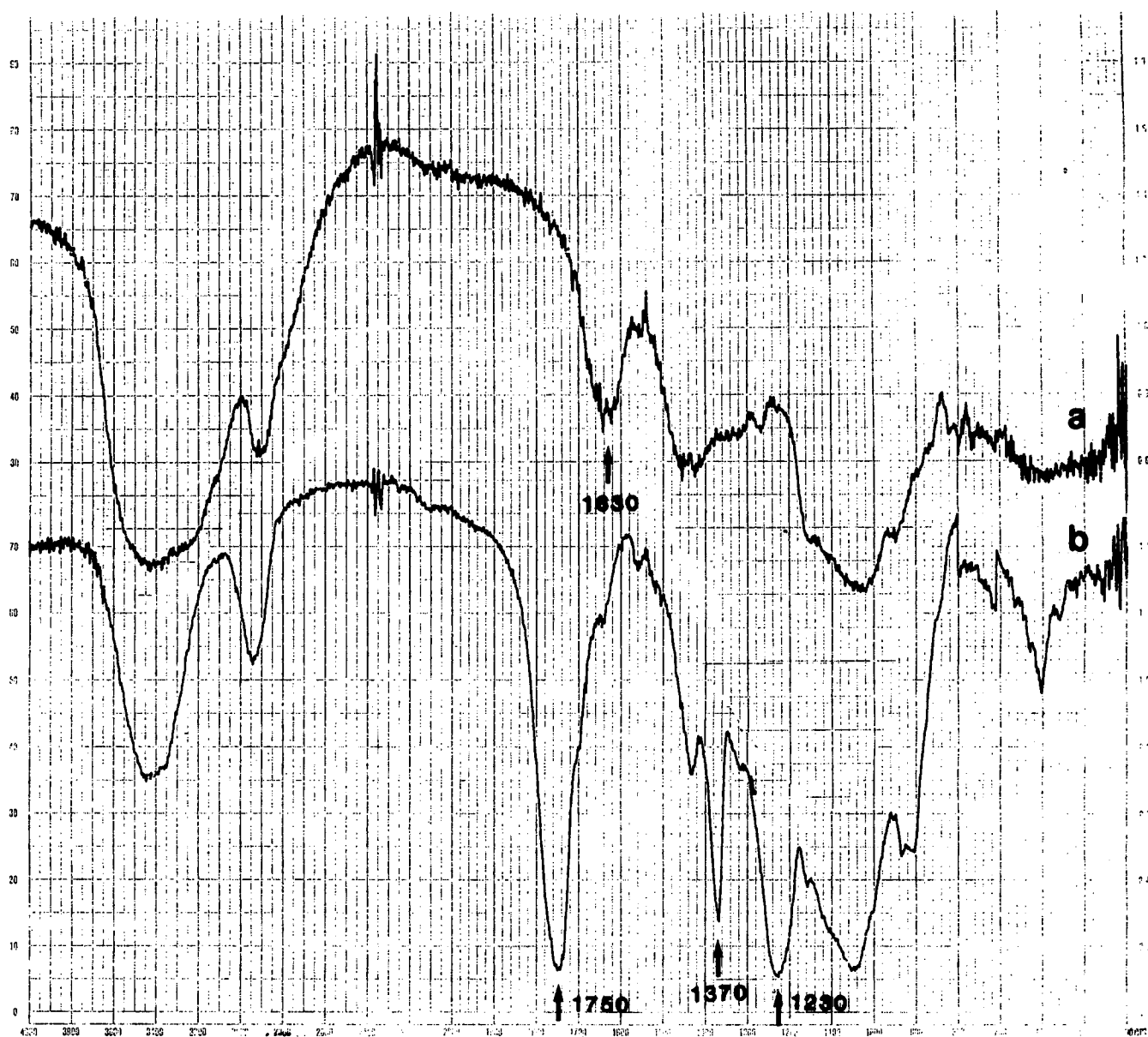


products, unfortunately we cannot conclude which structure of hemiacetal form of (2)-2 or hemialdal form of (2)-3 prevails as this condensation product. However, at least both structures may be possible depending on conditions of the preparation.

The elemental analyses and yields found in condensation product of dialdehyde cellulose and adipic acid dihydrazide at different pH values are given in Table III, and the possible structures of the product in this case are presented with the theoretical elemental compositions. From the results of yields re-

covered and nitrogen contents introduced, the most favorable pH condition of preparation is expected to be in the range of 5.0–5.5, and it cannot lead to conclude whether the expected structure is also hemialdal form of (3)-1 or hemiacetal form of (3)-2. In this case, dialdehyde cellulose reacts with only one molecular reagent to give a condensation product because of large molecular hydrazide reagent such as adipic acid dihydrazide.

IR spectra of condensation products obtained from dialdehyde cellulose and thiosemicarbazide,



**Figure 6** IR spectra of reaction products derived from acetic anhydride and dioxime prepared from dialdehyde cellulose.

dialdehyde cellulose and adipic acid dihydrazide, respectively, are shown in Figure 5. In the former, strong absorption based on  $\text{>NH}$  or  $\text{>N-NH}_2$  groups and absorption assigned to thioamide type are observed at near  $1600\text{ cm}^{-1}$  and  $1520\text{ cm}^{-1}$ , respectively. On the other hand, in the latter a strong absorption based on an acid amide type is observed at near  $1670$  and  $1540\text{ cm}^{-1}$ . These results imply that these absorptions resulted from the formation of nitrogen-containing condensation products.

### Nitrogen-Containing Derivatives from Dialdehyde Celluloses Prepared by Periodate Oxidation of Regenerated Celluloses

Dioximes were prepared from dialdehyde celluloses, which were obtained by periodate oxidation of cellulose regenerated from nonaqueous solvent system for cellulose. Reduction products of the dioxime were expected to give a product corresponding to the structure of (4)-1 as shown by Guthrie.<sup>1</sup> However, as shown in Table IV, the actual analytical data of nitrogen content was quite low value of 4.74%. This value is rather close to nitrogen content calculated on the assumption of the structure of (4)-2. Therefore, the structure of (4)-2 formed by introduction of one amino group per oxidized glucose unit may be considered to be rather reasonable from the theoretical value of elemental analysis.

### Treatment with Dioxime and Acetic Anhydride

Reaction products of dioxime and acetic anhydride in the presence of anhydrous sodium acetate, as shown in Table IV, gave a much lower nitrogen content (5.38%) than the value expected from the formation of the dinitrile (11.33%), which was described previously by Gal'braikh and Rogovin.<sup>9</sup> Also,

in the IR spectrum shown in Figure 6, an absorption of  $2210\text{--}2260\text{ cm}^{-1}$  assignable to nitrile groups,  $\text{-C}\equiv\text{N}$ , was not observed. Strong absorptions at  $1750$ ,  $1370$ , and  $1230\text{ cm}^{-1}$  caused by the formation of acetylated products were apparent. Thus, the acetylated product with the structure of (5)-2 is presumed. The actual nitrogen content (5.38%) found was value rather close to nitrogen content of 7.63% presumed as the structure of (5)-2. Therefore, this result means that the reaction of dioxime and acetic anhydride gives no dinitrile of the structure of (5)-1 formed by dehydration reaction reported by Gal'braikh et al.,<sup>9</sup> but acetylated product as shown in the structure of (5)-2.

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