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Note

^{13}C NMR determination of the distribution of two ester substituents in cellulose acetate butyrate *

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A cellulose ester derivative having two different substituents, namely, cellulose acetate butanoate (butyrate) (CAB) has been produced commercially for a wide variety of applications, such as molding plastics, film products, lacquer coatings, and melt coatings[1]. As the final properties of these products may be optimized through precise control of the distribution pattern of the two ester substituent groups on a glucose residue ("anhydroglucose unit") in addition to control of the relative and the total contents of the two substituents, a simple and reliable analytical method is of a significant importance both for elucidating structure–property relationships and for achieving quality control in production process.

We have recently proposed[2–7] a new analytical technique for cellulose derivatives, in particular cellulose ethers, in which unsubstituted hydroxyl groups on the anhydroglucose unit (and those at the end of substituent groups in some cases) are peracetylated and subjected to NMR measurements. We have demonstrated that the acetyl and other ester carbonyl carbon signals may be utilized as an extremely sensitive NMR probe for monitoring the substitution position on the anhydroglucose unit. Extending the preceding studies, we herein report a ^{13}C NMR determination of the distribution of acetyl and butanoyl (butyryl) substituents in commercial CAB samples.

A full-range ^{13}C NMR spectrum of a CAB sample is shown in Fig. 1. In addition to the signals for C-1–C-6 in the anhydroglucose unit, the methyl (doublet at 13.5 and 13.6 ppm) and methylene (doublet at 18.0 and 18.3 ppm, and doublet at 35.7 and 35.9 ppm) signals from the butyryl groups and the acetyl methyl signal (doublet at 20.4 and 20.6 ppm) were observed, and the relative contents of the two

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* Part 7 of a series ^{13}C NMR Structural Studies on Cellulose Derivatives with Carbonyl Groups as a Sensitive Probe. For part 6, see ref. 7.

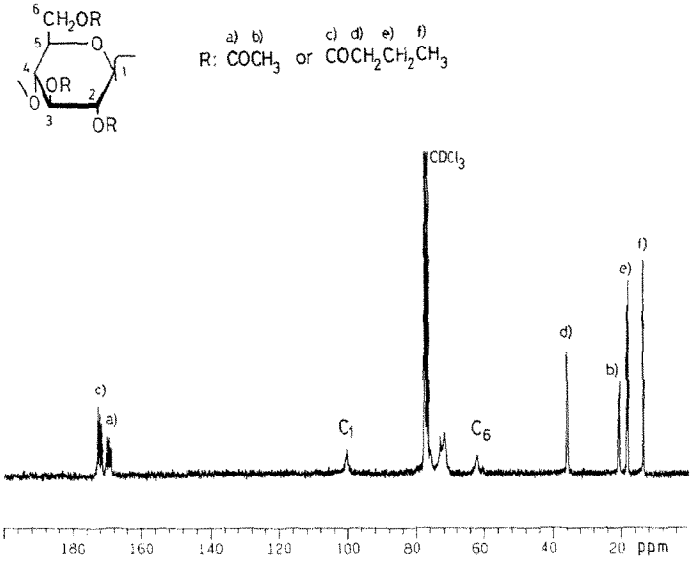


Fig. 1. ^{13}C NMR spectrum (67.8 MHz) of cellulose acetate butyrate (sample: CAB-381-0.5, $CDCl_3$, 40°C).

ester groups were determined by quantitative ^{13}C NMR measurements. The values obtained agreed with those obtained from analysis of the carbonyl region (see later).

A remarkable feature of the ^{13}C NMR spectra of a series of CAB samples is that both acetyl and butyryl carbonyl carbon signals appear seperately and are resolved into three peaks corresponding to their substitution positions on the anhydroglucose unit. The expanded carbonyl-region spectra of CAB samples having different acetyl and butyryl contents are shown in Fig. 2. The three peaks in the acetyl carbonyl region have been previously assigned, namely, at the 2 (169.0), 3 (169.5), and 6 (170.0 ppm) positions on the anhydroglucose unit[8].

Direct assignment of the three peaks in the butyryl carbonyl region[9,10] was achieved here by the INAPT technique[11] using a CAB sample of the highest butyryl content; the H-2 and H-3 proton signals were assigned by an H–H COSY measurement as shown in Fig. 3 and subsequently irradiated by a soft pulse to cause selective long-range polarization transfer to the carbonyl carbon of the butyryl groups. As summarized in Fig. 4, the INAPT spectra involving the irradiation of H-3 (5.11 ppm) and of H-2 (4.80 ppm) gave uniquely the signals at 172.1 and 171.6 ppm, respectively. This permits assignment of three butyryl carbonyl peaks, namely, at the 2 (171.6), 3 (172.1), and 6 (172.6 ppm) positions on the anhydroglucose unit.

The relative contents of acetyl and butyryl groups for a series of CAB samples were thus determined through quantitative-mode ^{13}C NMR measurements and the absolute distribution of the two substituents was subsequently determined by

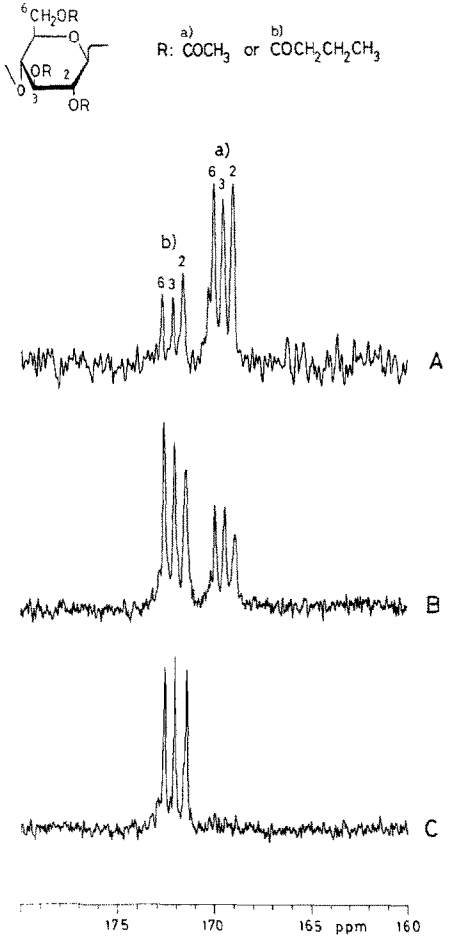


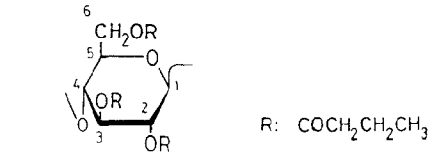
Fig. 2. ^{13}C NMR carbonyl-region spectra of cellulose acetate butyrate samples (samples: [A] CAB-171-15S, [B] CAB-381-0.5, [C] CAB-500-5, 67.8 MHz, $CDCl_3$, 40°C).

taking into account the total degrees of substitution of the CAB samples. The results obtained are collected in Table I. It may be noted that the degrees of substitution of the two ester substituents are close to each other at the 2, 3, and 6 positions in the present CAB samples, in particular in the sample 381-0.5.

In conclusion, the distribution pattern of the two ester substituents of a series of commercial CAB samples is readily determined by means of a ^{13}C NMR technique employing the ester carbonyl carbon as a remarkably sensitive NMR probe.

EXPERIMENTAL

Samples.—A series of cellulose acetate butyrate (CAB) samples, designated CAB-171-15S, CAB-381-0.5, and CAB-500-5 having total degrees of substitution of



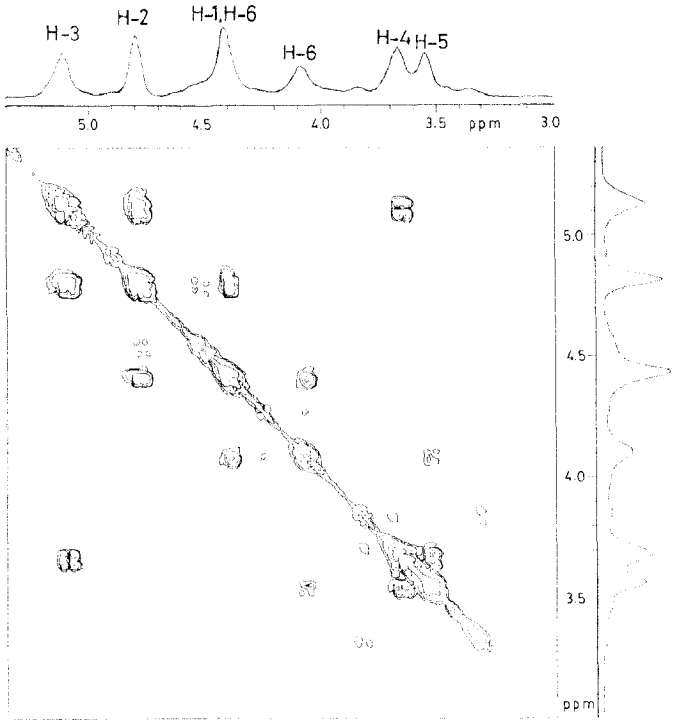


Fig. 3. H–H COSY spectrum of cellulose acetate butyrate of high butyryl content (sample: CAB-500-5, 400 MHz, $CDCl_3$, 40°C).

2.91, 2.66, and 3.01, respectively, were supplied by Eastman Chemical Japan Ltd., and were used as received. The total and respective contents of acetyl and butyryl groups, obtained by ^1H NMR measurements in Me_2SO-d_6 with the addition of a drop of trifluoroacetic acid, were supplied by Dr. J.A. Hyatt[12].

NMR spectra.—^1H and ^{13}C NMR measurements were performed with Jeol GX-270 or EX-400 spectrometers at 270 or 400 MHz for ^1H and 67.8 or 100 MHz for ^{13}C, respectively, with a 5-mm ϕ C-H dual probe, with solutions in $CDCl_3$ at 40°C. Chemical-shift values were referenced from the solvent signal of $CDCl_3$ (7.30 for ^1H and 77.0 ppm for ^{13}C). Quantitative-mode ^{13}C NMR measurements were performed by a non-NOE gated-decoupling technique with a pulse-repetition time of 30 s, and with ~ 2000 transients.

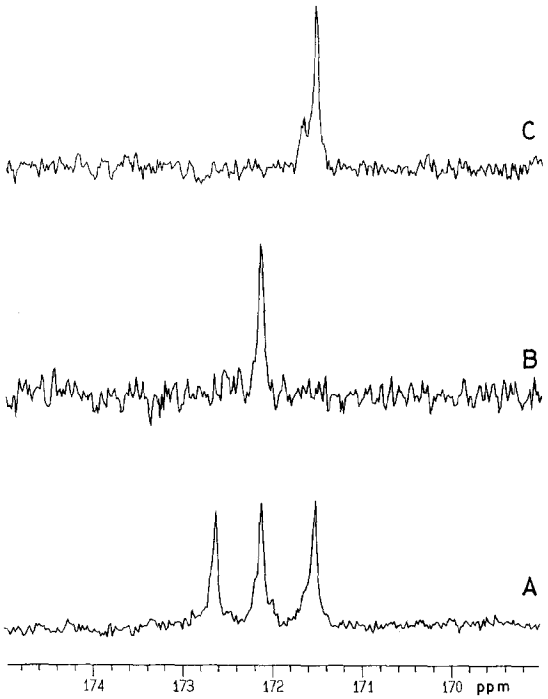


Fig. 4. Normal proton-decoupled ^{13}C NMR carbonyl-region spectrum of cellulose acetate butyrate of high butyryl content [A], the INAPT spectra with irradiation of H-3 [B], and of H-2 [C] (sample: CAB-500-5, 100 MHz, $CDCl_3$, 40°C).

A H–H COSY measurement was carried out by means of a Jeol EX-400 apparatus with a 1024×256 data matrix, and 4 transients were acquired for each t_1 value. A spectral width of 2698.3 Hz was used in both dimensions and a pulse delay of 1.31 s was used between scans. The spectrum was processed by using a sine-bell filtering function in both dimensions after zero-filling to a 1024×512 matrix.

INAPT (selective INEPT) measurements[11] were performed with a Jeol EX-400 apparatus. The delays $\Delta_1/2$ and $\Delta_2/2$ were both set to 40 ms, and the pulse width

TABLE I

Distribution of substituents in cellulose acetate butyrate samples

Sample code	$COCH_3$				$COCH_2CH_2CH_3$			
	2	3	6	Total	2	3	6	Total
171-15S	0.63	0.72	0.84	2.19 (2.14) [a]	0.33	0.25	0.13	0.71 (0.77) [a]
381-0.5	0.33	0.33	0.29	0.95 (0.97) [a]	0.56	0.56	0.59	1.71 (1.69) [a]
500-5	0.07	0.07	0.09	0.23 (0.29) [a]	0.93	0.93	0.91	2.77 (2.72) [a]

[a] From ^1H NMR analysis[12].

of the selective soft 90° ^1H pulse was set to 10 ms. Calibration of this 90° pulse was performed according to the pulse sequence of Bax[13] with incrementation of the attenuation using 90% ethylbenzene in CD_3COCD_3. The optimum value of the present system was found for an attenuation value of 445. Broad-band decoupling was applied during data acquisition and a pulse delay of 1.5 s was used between scans. Each of the INAPT spectra was obtained with $\sim 10^4$ transients.

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