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Analysis of the positions of substitution of acetate and butyrate groups in cellulose acetate–butyrate by the reductive-cleavage method

Nanxiong Yu, Gary R. Gray *

The Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, USA

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Abstract

The degree of substitution (ds) and the distribution pattern of the two ester substituents in commercial samples of cellulose acetate–butyrate (CAB) were determined by sequential neutral methylation, direct reductive cleavage and in situ acetylation. When the reductive-cleavage reaction was conducted with 35 equiv (per anhydroglucose unit) of Et_3SiH, 70 equiv of $MeSO_3SiMe_3$, and 14 equiv of $BF_3{\cdot}OEt_2$ at room temperature for seven days, the *O*-acetyl groups were converted to *O*-ethyl groups and the *O*-butyryl groups were converted to *O*-butyl groups concurrent with reductive cleavage of the glycosidic linkages. Acetylation of the products gave 27 partially methylated, ethylated, and butylated 4-*O*-acetyl-1,5-anhydro-D-glucitol derivatives that were identified by GLC–CIMS (NH_3) and GLC–EIMS. Integration of the GLC profile and correction for molar response gave the mole percent of each product. From these data, the fractional degree of substitution for each ester at each position of the anhydroglucose unit was determined. The combined fractional degree of substitution of both esters at each position and the overall ds were also determined by sequential neutral methylation, acyl–ethyl exchange, and reductive cleavage, and the values so obtained were in good agreement with those derived by sequential neutral methylation and direct reductive cleavage.

Keywords: Reductive-cleavage; Cellulose acetate–butyrate; Ester localization

1. Introduction

Cellulose acetate–butyrate (CAB) has been produced commercially for a wide variety of applications, such as molding plastics, film products, lacquer coatings, and melt coatings [1]. The functional properties of these products depend upon their degree of substitution (ds) as well as the distribution pattern of the two ester substituent groups on the (1→4)-β-D-glucopyranosyl residues of the polysaccharide. The structural characterization of cellulose acetate–butyrate samples is therefore of significant importance, both for elucidating structure–property relationships and for achieving quality control in production processes. Due to the presence of two different ester substituents, there are 27 possible monomeric anhydroglucose units with varying substituents at the 2-, 3-, and 6-positions. Although ^1H NMR spectroscopy has been

* Corresponding author. Fax: +1-612-626-7541; e-mail: gray@chem.umn.edu

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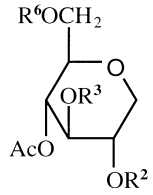
employed to determine the ds of each ester substituent [2] and ^{13}C NMR spectroscopy has been used to determine the fractional degree of substitution of each ester substituent at each position [3], no method has yet been reported for establishing the precise distribution pattern of the individual ester substituents, namely, the mole fractions of all 27 possible monomeric anhydroglucose units.

In a previous study [4] it was shown that the positions of substitution of *O*-acetyl groups in cellulose acetates could be established by sequential methylation under neutral conditions and direct reductive cleavage under conditions that reduced the *O*-acetyl groups to *O*-ethyl groups concurrent with reductive cleavage of glycosidic linkages. These results suggested that it might be possible to establish the distribution pattern of *O*-acetyl and *O*-butyryl groups in CAB by the same procedure. The 27 possible products so obtained (Table 1) should contain a single *O*-acetyl group (at the 4-position) and varying numbers of *O*-methyl, *O*-ethyl, and *O*-butyl groups. Separation and characterization of these products would reveal the fractional degree of substitution of each ester group at the 2-, 3-, and 6-positions of the 4-linked D-glucopyranosyl residues of the polysaccharide.

As a test of this procedure, two commercial samples of CAB were subjected to sequential neutral methylation and direct reductive cleavage, and the products were acetylated, separated by GLC, and characterized by mass spectrometry. In order to validate the method, the same CAB samples were subjected to sequential neutral methylation, acyl–ethyl exchange, and reductive cleavage and the eight products so obtained were separated by GLC and characterized as previously described [4]. The latter experiment was not capable of establishing the fractional degree of substitution of each ester at each position but could, for purposes of comparison, establish the combined fractional degrees of substitution of *both* esters at each position as well as the overall ds.

Table 1
Products derived from cellulose acetate–butyrate by sequential neutral methylation, direct reductive cleavage, and acetylation



Compound number	R^2	R^3	R^6	Parameter	Molecular weight
1	Me	Me	Me	S_0	248
2	Me	Et	Me	S_{3E}	262
3	Me	Me	Et	S_{6E}	262
4	Et	Me	Me	S_{2E}	262
5	Me	Et	Et	S_{36E}	276
6	Et	Et	Me	S_{23E}	276
7	Et	Me	Et	S_{26E}	276
8	Et	Et	Et	S_{236E}	290
9	Me	Bu	Me	S_{3B}	290
10	Me	Me	Bu	S_{6B}	290
11	Bu	Me	Me	S_{2B}	290
12	Me	Bu	Et	S_{3B6E}	304
13	Me	Et	Bu	S_{6B3E}	304
14	Et	Bu	Me	S_{3B2E}	304
15	Bu	Et	Me	S_{2B3E}	304
16	Bu	Me	Et	S_{2B6E}	304
17	Et	Me	Bu	S_{6B2E}	304
18	Et	Bu	Et	S_{3B26E}	318
19	Et	Et	Bu	S_{6B23E}	318
20	Bu	Et	Et	S_{2B36E}	318
21	Me	Bu	Bu	S_{36B}	332
22	Bu	Bu	Me	S_{23B}	332
23	Bu	Me	Bu	S_{26B}	332
24	Et	Bu	Bu	S_{36B2E}	346
25	Bu	Bu	Et	S_{23B6E}	346
26	Bu	Et	Bu	S_{26B3E}	346
27	Bu	Bu	Bu	S_{236B}	374

2. Results

Analysis of cellulose acetate–butyrate by methylation and direct reductive cleavage.—Two different samples of cellulose acetate–butyrate having similar ds values were chosen for analysis, one (sample A; Eastman CAB 381-20) having a low acetate:butyrate ratio (0.94:1.71) and the other (sample B; Eastman CAB 171-15S) having a high acetate:butyrate ratio (2.08:0.78). The samples were methylated by the method of Prehm [5], as described by Mischnick [6], and a portion of each was subjected to reductive cleavage at room temperature for seven days in the presence of 35 equiv (per anhydroglucose unit) of Et_3SiH, 70 equiv of $MeSO_3SiMe_3$, and 14 equiv of $BF_3{\cdot}OEt_2$. After quenching with anhydrous methanol, the products were acetylated in situ by treatment with acetic anhydride and 1-methylimidazole then analyzed by GLC and GLC combined with CIMS (NH_3) and EIMS. Shown in Figs. 1 and 2 are the gas–liquid chromatograms obtained when the products derived from samples A and B, respectively, were chromatographed on a Restek RT_x-200 column.

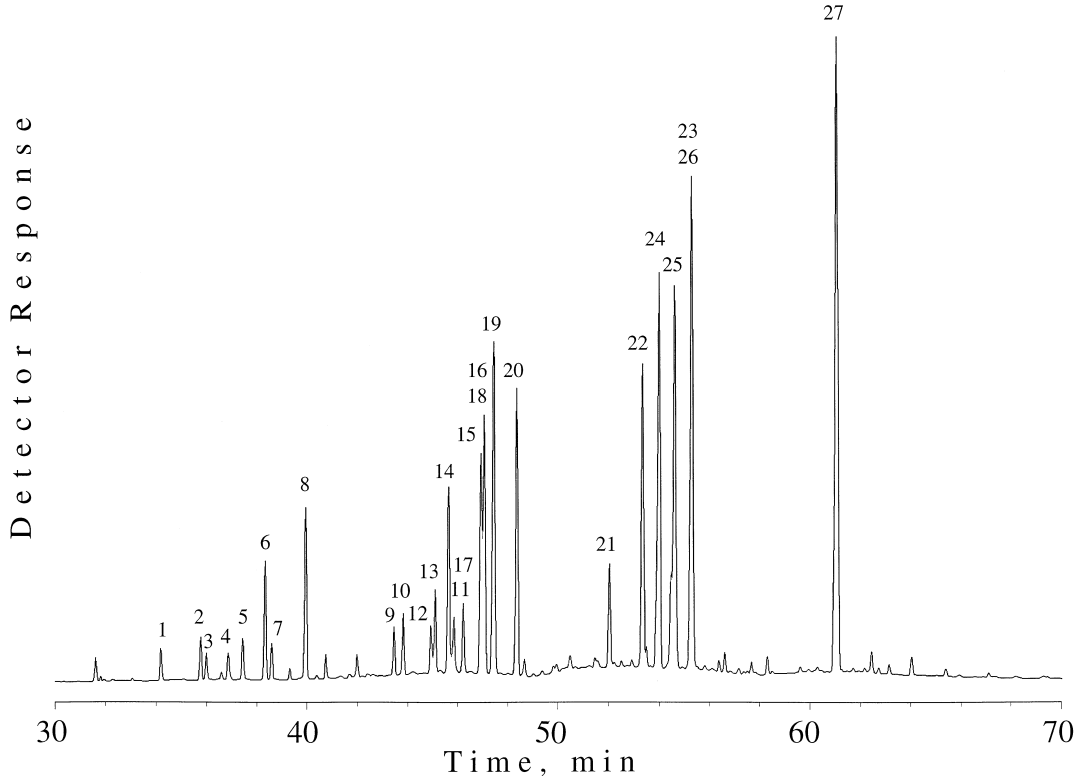


Fig. 1. Gas–liquid chromatogram of the anhydroalditol acetates derived from cellulose acetate–butyrate (Sample A) by sequential per-*O*-methylation, reductive cleavage and acetylation. Chromatography was conducted on a Restek RT_x-200 column. The peaks are numbered with the compound numbers.

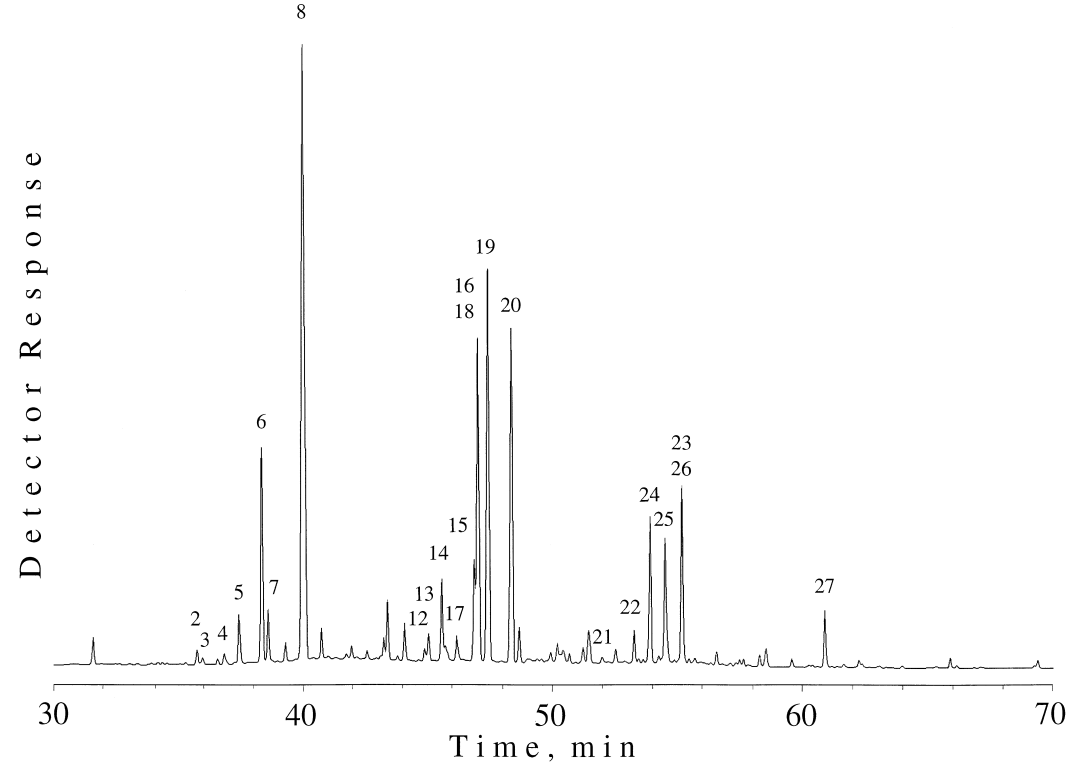


Fig. 2. Gas–liquid chromatogram of the anhydroalditol acetates derived from cellulose acetate–butyrate (Sample B) by sequential per-*O*-methylation, reductive cleavage and acetylation. Chromatography was conducted on a Restek RT_x-200 column. The peaks are numbered with the compound numbers.

The individual peaks were identified based on their molecular weights, as obtained by CIMS (NH_3), and their electron-ionization (EI) mass spectra (see discussion below). Integration of all peaks and correction for molar response by the effective carbon response method [7,8] gave the mole percent of each component in each of the samples (Table 2). Compounds **16** and **18** coeluted as did compounds **23** and **26**, but since the two components in each of the coeluting peaks possessed a different molecular weight, their relative proportions could be determined from the relative intensities of the (M + 1) peaks in the ammonia CI mass spectra of the mixtures.

It should also be noted that the gas–liquid chromatograms for the two CAB samples (Figs. 1 and 2) contained small amounts of products that could not be identified as 4-*O*-acetyl-1,5-anhydro-D-glucitol derivatives. Although the origin of these products is not known, it is possible that they arise from incomplete methylation of the CAB samples, incomplete reduction of esters to ethers during the reductive cleavage reaction, or from the sugar residues of non-cellulosic polysaccharides present in the starting materials for CAB preparation. Based on the excellent quantitative results obtained (see Discussion), their presence in such small amounts apparently does not affect the quantitative accuracy of the method.

Analysis of cellulose acetate–butyrate by methylation, acyl–ethyl exchange, and reductive cleavage.—Another portion of each fully methylated cellulose acetate–butyrate sample was subjected to acyl–ethyl exchange as previously described [4], and the products were then subjected to reductive cleavage at room temperature for 24 h in the presence of 5 equiv (per equiv of acetal) of Et_3SiH, 5 equiv of $MeSO_3SiMe_3$ and 1 equiv of $BF_3{\cdot}OEt_2$. Analysis of the products as their acetates on an RT_x-200 column revealed only eight peaks, corresponding to the same eight products (**1**–**8**) as derived from partially methylated cellulose acetate by sequential neutral methylation, acetyl–ethyl exchange, reductive cleavage and acetylation [4]. Integration of all peaks and correction for molar response [7,8] gave the mole percent of each product (**1**–**8**) in each sample of cellulose acetate–butyrate analyzed (Table 3). Using these values, the fractional degree of substitution (x_2, x_3 and x_6) at each of the three positions on the D-glucopyranosyl residues of cellulose and the average ds ($ds = x_2 + x_3 + x_6$) were calculated.

Table 2
Mol% of products derived by reductive cleavage of *O*-acetyl-*O*-butyryl-*O*-methyl cellulose

Compound number	Parameter	ECR value [a]	Mol%	
			Sample A [b]	Sample B [b]
1	S_0	0.545	0.71	–
2	S_{3E}	0.645	0.70	0.37
3	S_{6E}	0.645	0.56	0.15
4	S_{2E}	0.645	0.61	0.30
5	S_{36E}	0.745	0.61	1.18
6	S_{23E}	0.745	2.88	10.38
7	S_{26E}	0.745	0.58	1.63
8	S_{236E}	0.845	3.55	28.53
9	S_{3B}	0.845	1.00	–
10	S_{6B}	0.845	1.03	–
11	S_{2B}	0.845	1.23	–
12	S_{3B6E}	0.945	0.82	0.26
13	S_{6B3E}	0.945	1.73	0.41
14	S_{3B2E}	0.945	3.66	1.05
15	S_{2B3E}	0.945	2.82	3.23
16	S_{2B6E}	0.945	0.11	0.18
17	S_{6B2E}	0.945	1.48	0.71
18	S_{3B26E}	1.045	5.29	8.96
19	S_{6B23E}	1.045	7.37	13.44
20	S_{2B36E}	1.045	6.48	12.81
21	S_{36B}	1.145	1.84	0.16
22	S_{23B}	1.145	8.15	1.21
23	S_{26B}	1.145	2.34	1.57
24	S_{36B2E}	1.245	9.73	3.94
25	S_{23B6E}	1.245	10.30	4.13
26	S_{26B3E}	1.245	8.64	3.91
27	S_{236B}	1.445	15.78	1.48

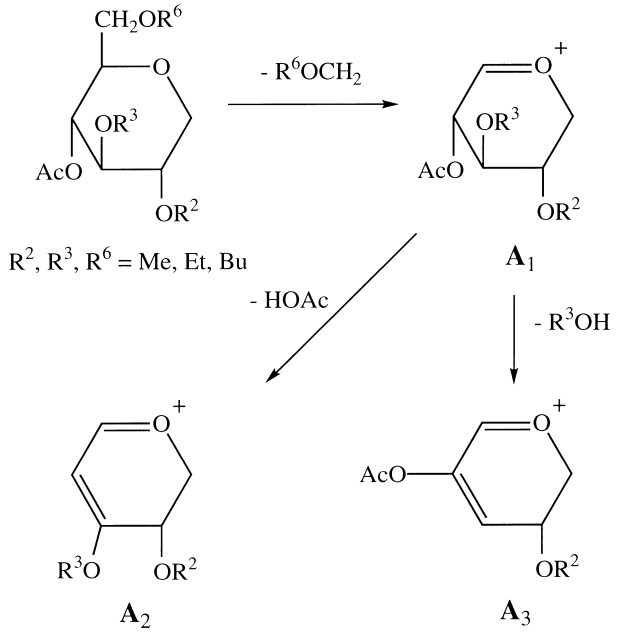
[a] Peak areas were divided by the indicated values in order to correct for molar response.
[b] A, Eastman CAB 381-20; B, Eastman CAB 171-15S.

Table 3
Mol% of products derived from cellulose acetate–butyrate by sequential neutral methylation, acyl–ethyl exchange, and acetylation and the fractional degrees of substitution of esters at the 2-, 3-, and 6-positions

Compound number	Parameter [a]	Mol%	
		Sample A [b]	Sample B [b]
1	S_0	0.38	–
2	S_{3E}	1.21	0.51
3	S_{6E}	1.75	0.50
4	S_{2E}	1.14	0.47
5	S_{36E}	4.98	3.52
6	S_{23E}	14.54	9.97
7	S_{26E}	5.69	3.71
8	S_{236E}	70.31	81.32
	x_2	0.92	0.96
	x_3	0.91	0.95
	x_6	0.82	0.89
	ds	2.65	2.80

[a] $x_2 = S_{2E} + S_{23E} + S_{26E} + S_{236E}$; $x_3 = S_{3E} + S_{23E} + S_{36E} + S_{236E}$; $x_6 = S_{6E} + S_{26E} + S_{36E} + S_{236E}$; $ds = x_2 + x_3 + x_6$.
[b] See footnote b, Table 2.

Identification of the partially methylated, ethylated, and butylated 1,5-anhydro-D-*glucitol acetates by mass spectrometry*.—Inspection of the EI mass spectra of compounds **1**–**27** revealed a fragmentation pathway (Scheme 1) identical to the one previously found for the related methyl/ethyl [9] and methyl/methoxycarbonylmethyl [10] positional isomers. The pathway begins by cleavage between C-5 and C-6 to give an $\mathbf{A}_1$ ion at (M−45), (M−59) and (M−87) for the 6-*O*-methyl, -ethyl and -butyl derivatives, respectively. Further elimination of acetic acid from the $\mathbf{A}_1$ ion gives an ion ($\mathbf{A}_2$) at (M−105), (M−119) and (M−147) for the 6-*O*-methyl, -ethyl and -butyl derivatives, respectively. The $\mathbf{A}_3$ ion, in contrast, is formed by elimination of methanol, ethanol or butanol from the $\mathbf{A}_1$ ion, and its molecular weight establishes the identity of the substituent at *O*-3. For example, 6-*O*-methyl derivatives give $\mathbf{A}_3$ ions at (M−77), (M−91) and (M−119) for 3-*O*-methyl, -ethyl and -butyl derivatives, respectively, whereas, 6-*O*-ethyl derivatives give $\mathbf{A}_3$ ions at (M−91), (M−105) and (M−133) for 3-*O*-methyl, -ethyl and -butyl derivatives, respectively. In contrast, 6-*O*-butyl derivatives give $\mathbf{A}_3$ ions at (M−119), (M−133) and (M−161) for 3-*O*-methyl, -ethyl and -butyl derivatives, respectively. For the benefit of those who might use this method, the molecular weights of these ions and their intensities relative to the base peak (*m*/*z* 43) are given in Table 4 for all positional isomers.



Scheme 1.

3. Discussion

Using the mole percents of products derived by reductive cleavage of *O*-acetyl-*O*-butyryl-*O*-methyl cellulose (Table 2), the fractional degree of substitution of each ester at each position of the anhydroglucose unit in the two CAB samples was calculated (Table 5, method 2). From these values the fractional degree of substitution of *both* esters at each position ($x_{2E}+x_{2B}$, $x_{3E}+x_{3B}$ and $x_{6E}+x_{6B}$, where E and B represent ethyl and butyl groups derived by reduction of acetyl and butyryl groups, respectively), the degree of substitution of each ester [ds (E) and ds (B)], and the overall degree of substitution of both esters [ds (E + B)] were also calculated (Table 5). As is evident by inspection of the data in Table 5, the values for the fractional degree of substitution of both esters at each position obtained by direct reductive cleavage of fully methylated CAB (method 2) are in excellent agreement with the values obtained by sequential methylation, acyl–ethyl exchange and reductive cleavage (method 1). Furthermore, the values obtained for the ds of each ester group by direct reductive cleavage of fully methylated CAB (method 2) were also in good agreement with those given by the supplier. The overall ds values obtained by sequential methylation, acyl–ethyl exchange and reductive cleavage (method 1) and by sequential methylation and direct reductive cleavage (method 2) were also in good agreement and, moreover, these values were also in good agreement with those given by the supplier. This is the only procedure yet developed for establishing the mole fractions of all 27 possible acetylated/butyrated anhydroglucose residues in CAB samples.

4. Experimental

Materials.—Cellulose acetate–butyrate samples were provided by Eastman Chemical Company, Kingsport, TN. Triethylsilane (Et_3SiH), trimethylsilyl methanesulfonate ($MeSO_3SiMe_3$), boron trifluoride etherate ($BF_3{\cdot}OEt_2$), methyl trifluoromethanesulfonate (CF_3SO_3Me) and 2,6 di-*tert*-butylpyridine were purchased from Aldrich Chemical Company and were used without further purification. Acetic anhydride was dried over 4 Å molecular sieves and distilled. 1-Methylimidazole was distilled from NaOH and stored over 4 Å molecular sieves. Trimethyl phosphate was distilled

Table 4
Characteristic fragment ions observed in the electron ionization mass spectra of compounds **1**–**27**

Compound Number	Parameter	Molecular weight	Fragment ions (m/z/% of Base peak [a])		
			A_1	A_2	A_3
1	S_0	248	203.1/13.15	143.1/25.44	171.0/25.27
2	S_{3E}	262	217.1/8.87	157.1/31.01	171.0/19.57
3	S_{6E}	262	203.1/19.20	143.0/35.02	171.0/35.42
4	S_{2E}	262	217.1/8.16	157.1/20.04	185.0/12.09
5	S_{36E}	276	217.1/13.27	157.1/26.48	171.0/28.77
6	S_{23E}	276	231.1/6.54	171.1/25.29	185.0/12.91
7	S_{26E}	276	217.1/6.84	157.1/8.95	185.0/13.66
8	S_{236E}	290	217.1/2.41	171.1/22.66	185.0/18.33
9	S_{3B}	290	245.1/7.24	185.1/36.77	171.0/27.92
10	S_{6B}	290	203.1/19.13	143.0/15.86	171.0/52.81
11	S_{2B}	290	245.1/7.83	185.1/21.10	213.1/8.90
12	S_{3B6E}	304	245.1/4.23	185.1/11.67	171.0/16.08
13	S_{6B3E}	304	217.1/16.15	157.1/24.55	171.0/49.50
14	S_{3B2E}	304	259.0/6.96	199.1/34.28	185.1/15.70
15	S_{2B3E}	304	259.1/6.40	199.1/31.78	213.1/10.23
16	S_{2B6E}	304	245.1/3.24	185.0/25.13	213.1/2.24
17	S_{6B2E}	304	217.1/7.12	157.1/15.46	185.0/12.39
18	S_{3B26E}	318	259.1/8.97	199.1/27.69	185.0/25.13
19	S_{6B23E}	318	231.1/11.84	171.1/30.71	185.1/26.49
20	S_{2B36E}	318	259.1/9.50	199.1/27.72	213.1/14.87
21	S_{36B}	332	245.1/14.20	185.1/31.75	171.0/58.76
22	S_{23B}	332	287.1/6.43	227.1/35.74	213.1/23.83
23	S_{26B}	332	245.1/5.02	185.1/2.86	213.1/17.85
24	S_{36B2E}	346	259.1/14.30	199.1/33.68	185.1/33.55
25	S_{23B6E}	346	287.1/8.82	227.1/32.49	213.1/20.15
26	S_{26B3E}	346	259.1/9.40	199.1/24.73	213.1/17.85
27	S_{236B}	374	287.1/8.00	227.1/26.12	213.1/19.29

[a] The base peak was at m/z 43 (CH_3CO^+) in all spectra.

Table 5
Fractional degree of substitution at the 2-, 3-, and 6-positions and the average degree of substitution in cellulose acetate–butyrate samples A and B [a]

Parameter[c]	Method 1 [b]		Method 2 [b]			
	Sample		Sample		Reported [d]	
	A	B	A	B	A	B
x_{2E}			0.35	0.69		
x_{2B}			0.56	0.28		
x_{3E}			0.35	0.74		
x_{3B}			0.57	0.21		
x_{6E}			0.28	0.58		
x_{6B}			0.50	0.26		
$x_{2E}+x_{2B}$	0.92	0.96	0.91	0.97		
$x_{3E}+x_{3B}$	0.91	0.95	0.92	0.95		
$x_{6E}+x_{6B}$	0.82	0.89	0.78	0.84		
ds (E)			0.98	2.01	0.94	2.08
ds (B)			1.63	0.75	1.71	0.78
ds (E + B)	2.65	2.80	2.61	2.76	2.65	2.86

[a] See footnote b, Table 2.
[b] Method 1: sequential methylation, acyl-ethyl exchange, reductive cleavage, and acetylation; Method 2: sequential methylation, direct reductive cleavage, and acetylation.
[c] $x_{2E}=S_{2E}+S_{23E}+S_{26E}+S_{236E}+S_{3B2E}+S_{6B2E}+S_{3B26E}+S_{6B23E}+S_{36B2E}$; $x_{2B}=S_{2B}+S_{2B3E}+S_{2B6E}+S_{2B36E}+S_{23B}+S_{26B}+S_{23B6E}+S_{26B3E}+S_{236B}$; $x_{3E}=S_{3E}+S_{36E}+S_{23E}+S_{236E}+S_{6B3E}+S_{2B3E}+S_{6B23E}+S_{2B36E}+S_{26B3E}$; $x_{3B}=S_{3B}+S_{3B6E}+S_{3B2E}+S_{3B26E}+S_{36B}+S_{23B}+S_{36B2E}+S_{23B6E}+S_{236B}$; $x_{6E}=S_{6E}+S_{36E}+S_{26E}+S_{236E}+S_{3B6E}+S_{2B6E}+S_{3B26E}+S_{2B36E}+S_{23B6E}$; $x_{6B}=S_{6B}+S_{6B3E}+S_{6B2E}+S_{6B23E}+S_{36B}+S_{26B}+S_{36B2E}+S_{26B3E}+S_{236B}$. ds (E) $=x_{2E}+x_{3E}+x_{6E}$. ds (B) $=x_{2B}+x_{3B}+x_{6B}$. ds (E + B) $=x_{2E}+x_{2B}+x_{3E}+x_{3B}+x_{6E}+x_{6B}$.
[d] Values given by the supplier.

from Na_2CO_3 under vacuum and stored over 4 Å molecular sieves. Dimethyl sulfoxide (Me_2SO) was distilled from barium oxide under vacuum and stored over 4 Å molecular sieves. Reagent grade methanol was refluxed over magnesium methoxide, distilled, and stored at room temperature over 4 Å molecular sieves under nitrogen. BioRad AG501-x8(D) was used as a mixed-bed resin.

Instrumentation.—Analytical GLC was performed on a Hewlett–Packard model 5890A gas–liquid chromatograph equipped with an on-column injector connected to a Restek RT_x-200 capillary column (0.25 mm × 30 m, 0.25-μm film thickness), a flame-ionization detector, and an HP model 3365 Series II ChemStation. The injector and detector temperatures were set at 250 and 275 °C, respectively, and the temperature of the column was programmed from 80 to 300 °C at 2 °C/min with no initial hold time. GLC–MS analyses were performed using a Finnegan MAT 95 high resolution double-focusing, reverse-geometry mass spectrometer equipped with a Hewlett–Packard 5890A Series II gas–liquid chromatograph and a DEC model 2100 workstation. Chemical ionization mass spectra were acquired with NH_3 as the reagent gas at a source temperature of 180 °C. Electron ionization mass spectra were obtained at an ionization energy of 70 eV and at a source temperature of 200 °C.

Methylation of cellulose acetate–butyrates.—Methylation was performed by the method of Prehm [5] using modifications of the procedure as described by Mischnick [6]. The sample of cellulose acetate–butyrate (~35 mg) was dissolved in trimethyl phosphate (3.5 mL) in a 10-mL screw-capped vial with a Teflon-faced septum, 2,6-di-*tert*-butylpyridine (250 μL) and CF_3SO_3Me (200 μL) were then added, and the vial was kept at 45–50 °C in a small ultrasonic bath for 2 days. The reaction solution typically turned brown. After cooling to room temperature, the methylated product was precipitated by the addition of two volumes of water and the precipitate was collected by filtration through a small fritted disc. The precipitate was washed thoroughly with water then dissolved in chloroform and the chloroform extract was dried over anhydrous Na_2SO_4 and evaporated to dryness.

Reductive cleavage and in situ acetylation.—Fully methylated cellulose acetate–butyrate (~2 mg) was dissolved in CH_2Cl_2 (250 μL) in a 3-mL screw-capped, conical vial, Et_3SiH (37 μL), $MeSO_3SiMe_3$ (72 μL) and $BF_3{\cdot}OEt_2$ (12 μL) were sequentially added, the vial was capped with a mininert valve, and the solution was stirred at room temperature for seven days. The reaction was quenched by the addition of methanol (30 L), and the solution was stirred for 30 min. After cooling in an ice bath, acetic anhydride (250 μL) and 1-methylimidazole (100 μL) were added, and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was then extracted sequentially with saturated aqueous $NaHCO_3$, 2 N H_2SO_4 and H_2O. The organic layer was dried over anhydrous sodium sulfate then evaporated to dryness under a stream of nitrogen. The residue was dissolved in CH_2Cl_2 and examined by GLC.

Acknowledgements

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