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Analysis of the positions of substitution of acetate and propionate groups in cellulose acetate–propionate 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–propionate (CAP) 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*-propionyl groups were converted to *O*-propyl groups concurrent with reductive cleavage of the glycosidic linkages. Acetylation of the products gave 27 partially methylated, ethylated, and propylated 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–propionate; Ester localization

1. Introduction

Cellulose acetate–propionate (CAP) has been produced commercially for a wide variety of applications, such as printing inks, hot-melt dip coatings, lacquer coatings, and desalination membranes [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–propionate samples is therefore of significant importance, both for elucidating structure–property relationships and for achieving quality control in production

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

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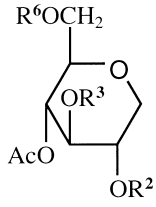
processes. The distribution patterns of acetyl and propionyl groups in CAP samples have not previously been established. In related work, however, the positions of substitution of *O*-acetyl and *O*-butyryl groups in cellulose acetate–butyrates were established by sequential methylation under neutral conditions and direct reductive cleavage under conditions that reduced the *O*-acetyl and *O*-butyryl groups to *O*-ethyl and *O*-butyl groups, respectively, concurrent with reductive cleavage of glycosidic linkages [2]. From these results it was obvious that it should be possible to establish the distribution pattern of *O*-acetyl and *O*-propionyl groups in CAP samples using the same procedure. The 27 possible products so obtained (Table 1), which contain a single *O*-acetyl group (at the 4-position) and varying numbers of *O*-methyl, *O*-ethyl, and *O*-propyl groups, were separated and characterized, revealing the fractional degree of substitution of each ester group at each position of the 4-linked D-glucopyranosyl residues of the polysaccharide. The same CAP samples were subjected to sequential neutral methylation, acyl–ethyl exchange, and reductive cleavage, and the eight products so obtained were separated by GLC and identified as previously described [3]. 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–propionate 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	Pr	Me	S_{3P}	276
10	Me	Me	Pr	S_{6P}	276
11	Pr	Me	Me	S_{2P}	276
12	Me	Pr	Et	S_{3P6E}	290
13	Me	Et	Pr	S_{6P3E}	290
14	Et	Pr	Me	S_{3P2E}	290
15	Pr	Et	Me	S_{2P3E}	290
16	Pr	Me	Et	S_{2P6E}	290
17	Et	Me	Pr	S_{6P2E}	290
18	Et	Pr	Et	S_{3P26E}	304
19	Et	Et	Pr	S_{6P23E}	304
20	Pr	Et	Et	S_{2P36E}	304
21	Me	Pr	Pr	S_{36P}	304
22	Pr	Pr	Me	S_{23P}	304
23	Pr	Me	Pr	S_{26P}	304
24	Et	Pr	Pr	S_{36P2E}	318
25	Pr	Pr	Et	S_{23P6E}	318
26	Pr	Et	Pr	S_{26P3E}	318
27	Pr	Pr	Pr	S_{236P}	332

2. Results

Analysis of cellulose acetate–propionate by methylation and direct reductive cleavage.—Three different samples of cellulose acetate–propionate having similar ds values were chosen for analysis, one (sample A: Eastman CAP 141-20) having a high acetate:propionate ratio (1.96: 0.69) and the other two (sample B: Eastman CAP 482-20 and sample C: Eastman CAP 504-02) having very low acetate:propionate ratios (0.01: 2.71 and 0.06: 2.16, respectively). The samples were methylated by the method of Prehm [4], as described by Mischnick [5], 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. 1–3 are the gas–liquid chromatograms obtained when the products derived from samples A, B, and C, respectively, were chromatographed on a Restek RT_x-200 column. The individual peaks were identified based on their molecular weights, as obtained by CIMS (NH_3), and their electron-ionization mass spectra (see discussion below). Integration of all peaks and correction for molar response by the effective carbon response method [6,7] gave the mole percent of each component in each of the samples (Table 2). Compounds **12** and **13** coeluted, and since they

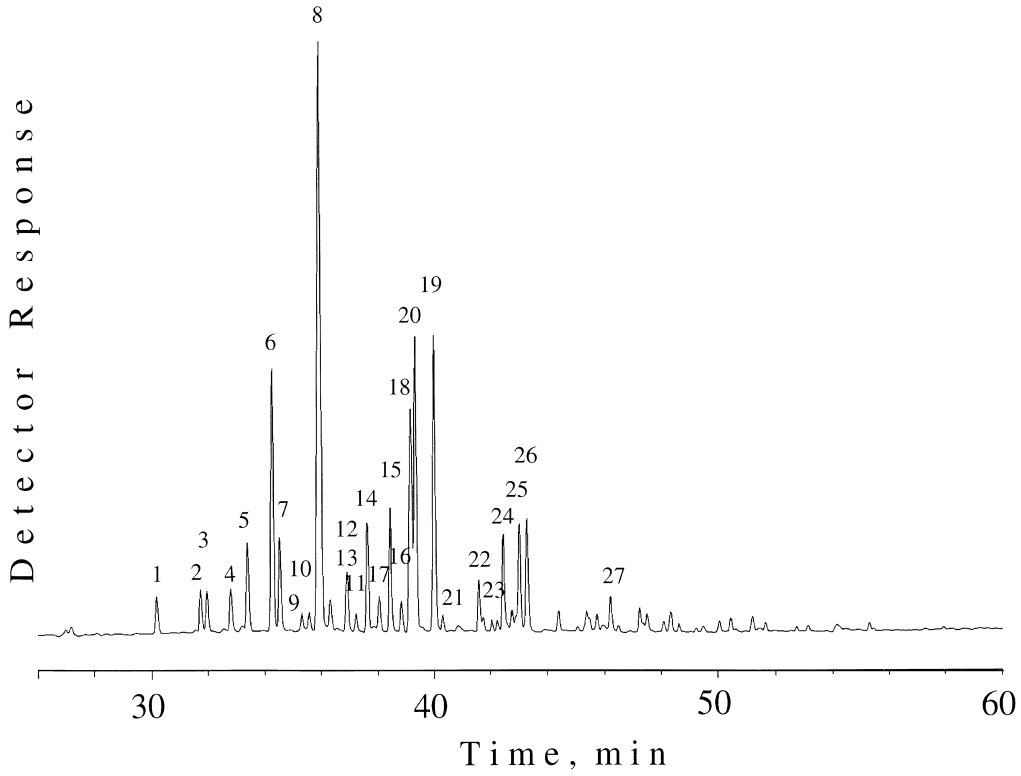


Fig. 1. Gas–liquid chromatogram of the anhydroalditol acetates derived from cellulose acetate–propionate (Sample A) by sequential per-*O*-methylation, reductive cleavage and acetylation. Chromatography was conducted on a Restek RT_x-200 column. The peaks are numbered with the compound numbers.

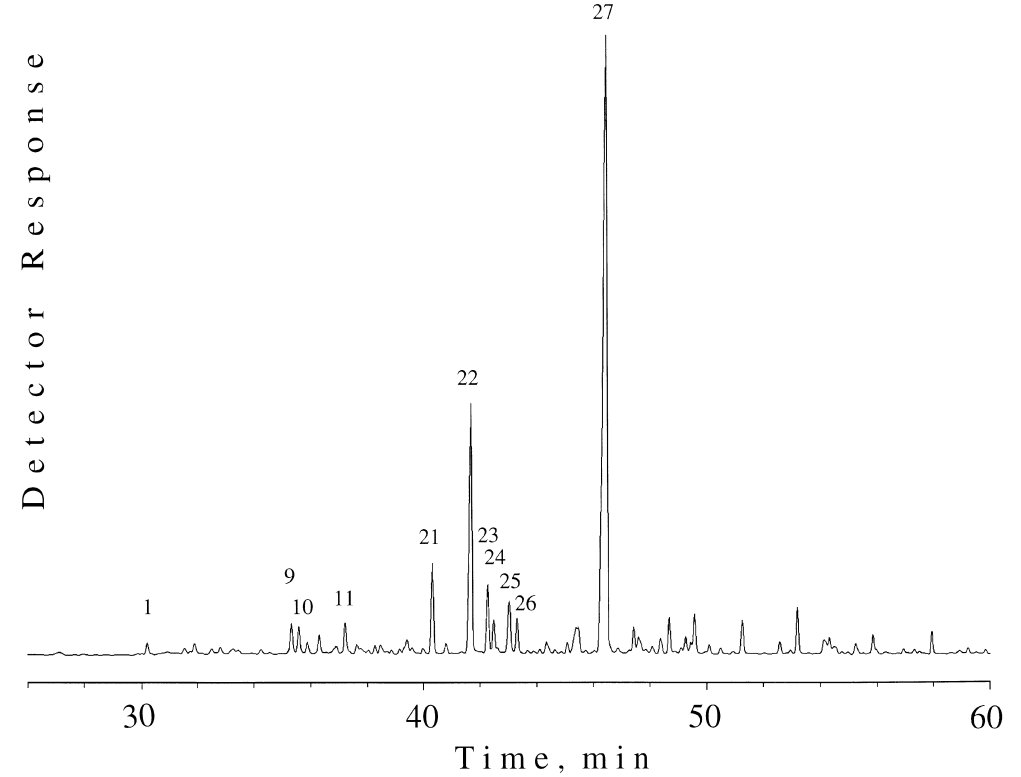


Fig. 2. Gas–liquid chromatogram of the anhydroalditol acetates derived from cellulose acetate–propionate (Sample B) by sequential per-*O*-methylation, reductive cleavage and acetylation. Chromatography was conducted on a Restek RT_x-200 column. The peaks are numbered with the compound numbers.

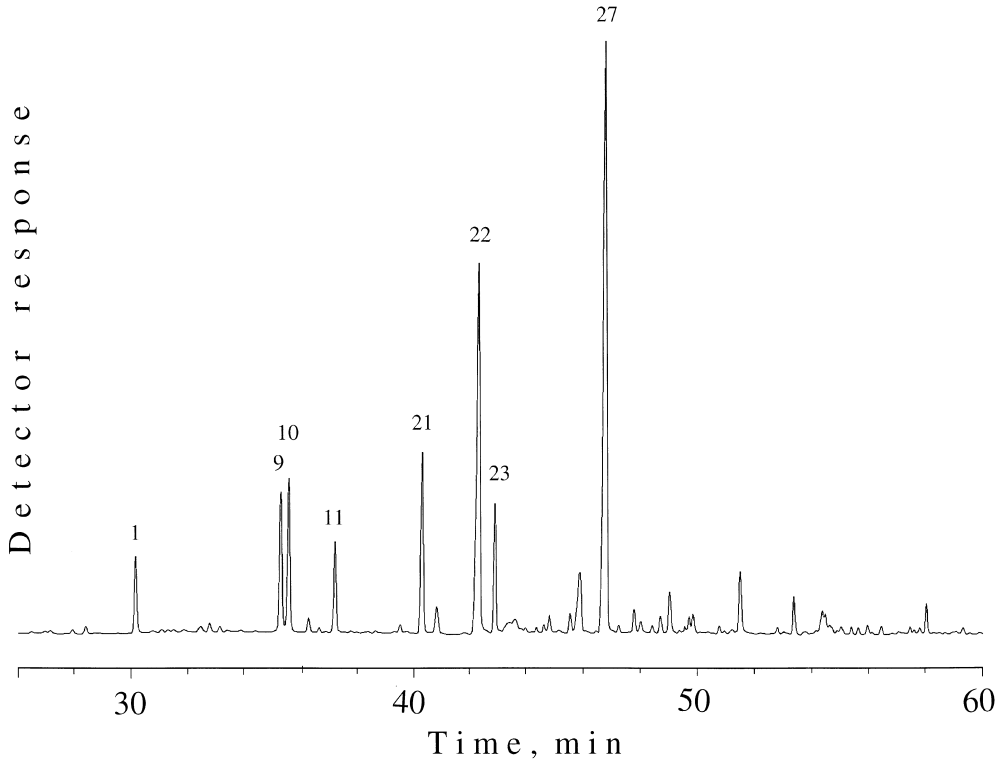


Fig. 3. Gas–liquid chromatogram of the anhydroalditol acetates derived from cellulose acetate–propionate (Sample C) by sequential per-*O*-methylation, reductive cleavage and acetylation. Chromatography was conducted on a Restek RT_x-200 column. The peaks are numbered with the compound numbers.

possessed the same molecular weight, their relative proportions were determined from the relative intensities of the $\mathbf{A}_1$ ions in their electron-ionization mass spectra.

It should also be noted that the gas–liquid chromatograms for the three CAP samples (Figs. 1–3) 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 CAP 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–propionate by methylation, acyl–ethyl exchange, and reductive cleavage.—Another portion of each fully methylated cellulose acetate–propionate sample was subjected to acyl–ethyl exchange as previously described [3], 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 [3]. Integration of all peaks and correction for molar response [6,7] gave the mole percent of each product (**1**–**8**) in each sample of cellulose acetate–propionate 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.

Identification of the partially methylated, ethylated, and propylated 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 [8], methyl/methoxycarbonylmethyl [9] and methyl/ethyl/butyl [2] 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−73) for the

Table 2
Mol% of products derived by reductive cleavage of *O*-acetyl-*O*-propionyl-*O*-methylcellulose

Compound number	Parameter	ECR value [a]	Mol%		
			Sample A [b]	Sample B [b]	Sample C [b]
1	S_0	0.545	1.63	0.17	2.98
2	S_{3E}	0.645	1.51		
3	S_{6E}	0.645	1.48		
4	S_{2E}	0.645	1.47		
5	S_{36E}	0.745	2.69		
6	S_{23E}	0.745	9.23		
7	S_{26E}	0.745	2.81		
8	S_{236E}	0.845	26.96		
9	S_{3P}	0.745	0.31	1.63	6.75
10	S_{6P}	0.745	0.31	1.34	8.24
11	S_{2P}	0.745	0.18	1.68	4.28
12	S_{3P6E}	0.845	0.99		
13	S_{6P3E}	0.845	1.21		
14	S_{3P2E}	0.845	3.16		
15	S_{2P3E}	0.845	3.76		
16	S_{2P6E}	0.845	0.28		
17	S_{6P2E}	0.845	0.28		
18	S_{3P26E}	0.945	7.57		
19	S_{6P23E}	0.945	9.69		
20	S_{2P36E}	0.945	8.88		
21	S_{36P}	0.945	0.12	4.98	8.18
22	S_{23P}	0.945	0.93	20.61	27.86
23	S_{26P}	0.945	0.22	3.88	6.98
24	S_{36P2E}	1.045	3.58	1.73	
25	S_{23P6E}	1.045	4.92	2.33	
26	S_{26P3E}	1.045	5.41	1.88	
27	S_{236P}	1.145	0.40	59.77	34.74

[a] Peak areas were divided by the indicated values in order to correct for molar response.
[b] A, Eastman CAP 141-20; B, Eastman CAP 482-20; C, Eastman CAP 504-02.

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

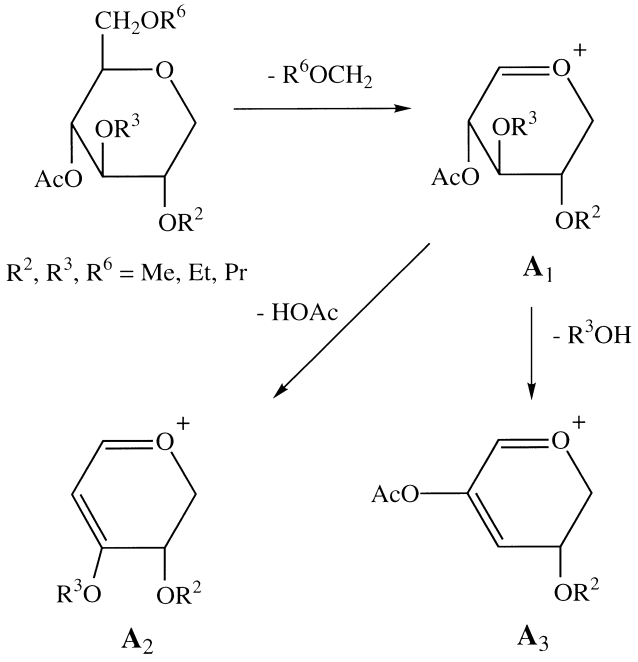
Compound number	Parameter [a]	Mol%		
		Sample A [b]	Sample B [b]	Sample C [b]
1	S_0	0.42	0.24	2.84
2	S_{3E}	1.32	1.00	4.34
3	S_{6E}	1.80	1.35	7.33
4	S_{2E}	1.40	0.87	3.47
5	S_{36E}	5.46	4.95	8.45
6	S_{23E}	16.06	13.34	21.74
7	S_{26E}	6.18	5.22	7.97
8	S_{236E}	67.36	73.02	43.86
	x_2	0.910	0.925	0.770
	x_3	0.902	0.923	0.784
	x_6	0.808	0.846	0.676
	ds	2.62	2.69	2.23

[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 $= x_2 + x_3 + x_6$.

6-*O*-methyl, -ethyl and -propyl 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−133) for the 6-*O*-methyl, -ethyl and -propyl derivatives, respectively. The $\mathbf{A}_3$ ion, in contrast, is formed by elimination of methanol, ethanol or propanol 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−105) for 3-*O*-methyl, -ethyl and -propyl derivatives, respectively, whereas, 6-*O*-ethyl derivatives give $\mathbf{A}_3$ ions at (M−91), (M−105) and (M−119) for 3-*O*-methyl, -ethyl and -propyl derivatives, respectively. In contrast, 6-*O*-propyl derivatives give $\mathbf{A}_3$ ions at (M−105), (M−119) and (M−133) for 3-*O*-methyl, -ethyl and -propyl 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.

3. Discussion

Using the mole% of products derived by reductive cleavage of *O*-acetyl-*O*-propionyl-*O*-methylcellulose (Table 2), the fractional degrees of substitution of each ester at each position of the anhydroglucose unit in the three CAP samples were calculated (Table 5, method 2). From these values the fractional degree of substitution of *both* esters at each position ($x_{2E} + x_{2P}$, $x_{3E} + x_{3P}$ and $x_{6E} + x_{6P}$, where E and P represent ethyl and propyl groups derived by reduction of acetyl and propionyl groups, respectively), the degree of substitution of each ester {ds (E) and ds (P)}, and the overall degree of substitution of both esters {ds (E + P)} were also calculated (Table 5). For sample A, which has a relatively high ds and substantial amounts of both acetyl and propionyl groups, the values obtained for the fractional degrees of substitution of both esters at each position using method 2 (sequential methylation, direct reductive cleavage, and acetylation) were in excellent agreement with those obtained by method 1 (sequential methylation, acyl–ethyl exchange, reductive cleavage and acetylation). Moreover, the overall ds values obtained for sample A by the two methods were in good agreement, and these values, as well as the individual ds values for acetyl and propionyl groups (obtained by method 2), were in



Scheme 1.

good agreement with those given by the supplier. For samples B and C, which also have relatively high ds values but contain only trace amounts of *O*-acetyl groups, the ds values obtained by method 1 were in excellent agreement with those given by the supplier. For these samples, however, the ds values obtained by method 2 were slightly lower than those obtained by method 1 and, in both cases, the major cause of the discrepancy was the lower-than-expected values for the fractional degree of substitution of both esters at the 6-position ($x_{6E}+x_{6P}$); the reason for this discrepancy is not known. In spite of the lower-than-expected ds values obtained for samples B and C by method 2, these two samples were readily distinguishable. No *O*-acetyl groups were detected in sample C so, if present, they must be distributed amongst the possible positional isomers at levels too low to detect. Sample B, however, was found to contain small quantities of *O*-acetyl groups at all three positions (Tables 2 and 5) and, interestingly, the *O*-acetyl

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	217.1/13.73	157.1/11.31	185.0/10.56
5	S_{36E}	276	217.1/17.56	157.1/36.49	171.0/37.93
6	S_{23E}	276	231.1/12.11	171.1/42.82	185.1/21.29
7	S_{26E}	276	217.1/12.61	157.1/21.89	185.1/23.79
8	S_{236E}	290	231.1/17.32	171.1/36.10	185.1/28.67
9	S_{3P}	276	231.1/14.16	171.1/9.84	171.1/9.84
10	S_{6P}	276	203.1/7.24	143.1/31.46	171.1/48.01
11	S_{2P}	276	231.1/13.21	171.1/37.58	199.1/19.37
12	S_{3P6E}	290	231.1/7.16	171.1/44.95	171.1/44.95
13	S_{6P3E}	290	217.1/9.40	157.1/23.37	171.1/44.95
14	S_{3P2E}	290	245.1/9.19	185.1/53.29	185.1/53.29
15	S_{2P3E}	290	245.1/8.86	185.1/29.01	199.1/12.77
16	S_{2P6E}	290	231.1/10.18	171.1/19.00	199.1/17.06
17	S_{6P2E}	290	217.1/16.18	157.1/31.55	185.1/29.54
18	S_{3P26E}	304	245.1/12.20	185.1/54.86	185.1/54.86
19	S_{6P23E}	304	231.1/16.60	171.1/26.26	185.1/26.17
20	S_{2P36E}	304	245.1/12.14	185.1/30.66	199.1/19.50
21	S_{36P}	304	231.1/22.56	171.1/92.51	171.1/92.51
22	S_{23P}	304	259.1/10.96	199.1/65.95	199.1/65.95
23	S_{26P}	304	231.1/14.33	171.1/24.79	199.1/30.85
24	S_{36P2E}	318	245.1/13.76	185.1/46.58	185.1/46.58
25	S_{23P6E}	318	259.1/8.64	199.1/37.98	199.1/37.98
26	S_{26P3E}	318	245.1/7.66	185.1/16.59	199.1/14.39
27	S_{236P}	332	259.1/6.58	199.1/30.81	199.1/30.81

[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–propionates[a]

Parameter [c]	Method 1[b]			Method 2[b]					
	Sample			Sample			Reported [d]		
	A	B	C	A	B	C	A	B	C
x_{2E}				0.648	0.017	0			
x_{2P}				0.250	0.902	0.738			
x_{3E}				0.694	0.019	0			
x_{3P}				0.220	0.910	0.775			
x_{6E}				0.566	0.023	0			
x_{6P}				0.212	0.736	0.581			
$x_{2E}+x_{2P}$	0.910	0.925	0.770	0.898	0.919	0.738			
$x_{3E}+x_{3P}$	0.902	0.923	0.784	0.914	0.929	0.775			
$x_{6E}+x_{6P}$	0.808	0.846	0.676	0.778	0.759	0.581			
ds(E)				1.91	0.06	0	1.96	0.01	0.06
ds(P)				0.68	2.55	2.09	0.69	2.71	2.16
ds(E + P)	2.62	2.69	2.23	2.59	2.61	2.09	2.65	2.72	2.22

[a] See footnote b, Table 2.
[b] Method 1: sequential methylation, acyl–ethyl exchange, reduction cleavage, and acetylation. Method 2: sequential methylation, direct reductive cleavage, and acetylation.
[c] $x_{2E}=S_{2E}+S_{23E}+S_{26E}+S_{236E}+S_{3P2E}+S_{6P2E}+S_{3P26E}+S_{6P23E}+S_{36P2E}$; $x_{2P}=S_{2P}+S_{2P3E}+S_{2P6E}+S_{2P36E}+S_{23P}+S_{26P}+S_{23P6E}+S_{26P3E}+S_{236P}$; $x_{3E}=S_{3E}+S_{36E}+S_{23E}+S_{236E}+S_{6P3E}+S_{2P3E}+S_{6P23E}+S_{2P36E}+S_{26P3E}$; $x_{3P}=S_{3P}+S_{3P6E}+S_{3P2E}+S_{3P26E}+S_{36P}+S_{23P}+S_{36P2E}+S_{23P6E}+S_{236P}$; $x_{6E}=S_{6E}+S_{36E}+S_{26E}+S_{236E}+S_{3P6E}+S_{2P6E}+S_{3P26E}+S_{2P36E}+S_{23P6E}$; $x_{6P}=S_{6P}+S_{6P3E}+S_{6P2E}+S_{6P23E}+S_{36P}+S_{26P}+S_{36P2E}+S_{26P3E}+S_{236P}$; $ds(E)=x_{2E}+x_{3E}+x_{6E}$; $ds(P)=x_{2P}+x_{3P}+x_{6P}$; $ds(E+P)=x_{2E}+x_{2P}+x_{3E}+x_{3P}+x_{6E}+x_{6P}$.
[d] Values given by the supplier.

groups detected in sample B were on residues that were otherwise fully propionylated (Table 2).

From these results it is concluded that sequential methylation under neutral conditions, reductive cleavage under conditions that reduce esters to ethers concomitant with reductive cleavage of glycosides, and acetylation is a valid procedure for establishing the mole fractions of the 27 possible acetylated/propionylated anhydroglucose residues in CAP samples.

4. Experimental

Materials.—Cellulose acetate–propionate samples were provided by Eastman Chemical Company, Kingsport, TN, USA. All reagents were obtained and purified as previously described [2].

Instrumentation.—Analytical GLC was performed on a Hewlett–Packard model 5890A gas–liquid chromatograph using the same columns and conditions as previously described [2]. 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 (EI) mass spectra were obtained at an ionization energy of 70 eV and at a source temperature of 200 °C.

Methylation and reductive cleavage.—Methylation was performed by the method of Prehm [4] using modifications of the procedure as described by Mischnick [5]. The conditions were the same as previously described for cellulose acetate–butyrate samples [2]. Reductive cleavage and in situ acetylation were also performed exactly as described for cellulose acetate–butyrate samples [2].

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