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Mass spectrometric studies of the thermal decomposition of carbohydrates using ^{13}C-labeled cellulose and glucose

Robert J. Evans [a], Dingneng Wang [a,*], Foster A. Agblevor [a], Helena L. Chum [a], Sheryl D. Baldwin [b]

[a] *Industrial Technologies Division, National Renewable Energy Laboratory, Golden, CO 80401, USA*
[b] *Philip Morris Research Center, Philip Morris USA, Richmond, VA 23261, USA*

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Abstract

The mechanism of the thermal decomposition of carbohydrates is very important to the development of fuels, fibers, and paper products. To help gain more insight into the pyrolysis chemistry of cellulose, we have carried out experimental studies using *Acetobacter xylinum* cellulose grown on D-(1-^{13}C)-glucose medium with incorporation levels of 1-^{13}C of 14%, as determined by ^{13}C NMR analysis. Samples of the labeled cellulose, as well as D-(1-^{13}C)- and D-(2-^{13}C)-glucose, were pyrolyzed under fast-heating conditions and the products analyzed by molecular beam mass spectrometry (MBMS). From the labeled cellulose samples, statistically significant levels of enrichment were observed for the pyrolysis products that occur at m/z 110, 114, 126, 144, and 191, but not at m/z 98, 60, or 31. The lack of enrichment in the latter fragments indicates that they do not incorporate C-1. Samples were treated with 0.1% aqueous KOH to favor the formation of glycolaldehyde, but even in this case this major product was not enriched. These results suggest that the m/z 60 ion is an EI fragment ion of levoglucosan, formed by loss of neutral species containing C-1. However, the m/z 191 ion was found to contain two C-1 carbons. Collision-induced dissociation results for this ion suggest that it consists of a formate group. The structure of this ion is proposed to be the protonated formate of levoglucosan at the C-4 position, derived from either a reverse aldol reaction or a ±-Diels–Alder reaction. The (1-^{13}C)-glucose pyrolysis product distribution is similar to that for (1-^{13}C)-labeled cellulose. The (2-^{13}C)-glucose pyrolysis product distribution shows significant contribution from C-2 at the M + 1 peaks of m/z 32, 43, 60, 73, 85, and 97, indicating major incorporations of C-2 in glycolaldehyde in contrast to the lack of incorporation of the C-1 position in this major product.

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[*] Corresponding author.

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1. Introduction

Cellulose pyrolysis has been extensively studied because of its significance in many areas of industrial importance. Early studies focused on topics such as the effect of crystallinity, the mechanism of levoglucosan formation, the effect of inorganic material, and the existence of other major pathways besides levoglucosan formation [1–4]. Recent work has identified glycolaldehyde as a major product of cellulose pyrolysis [5,6]. The mechanisms by which low-molecular-weight products such as glycolaldehyde and acetic acid are formed from cellulose pyrolysis remain questions of great importance. Gaining insight into these mechanisms is the purpose of this work.

Among the most frequently proposed mechanisms for the formation of small molecules from cellulose pyrolysis are homolytic fragmentation pathways that involve radical intermediates [7], reverse aldol reactions [8], heterolytic fragmentation via either cationic or anionic intermediates [9–11], and ±-Diels–Alder reactions [6,12,13], such as a [2 + 2 + 2] concerted fragmentation of the glucose ring to form three molecules of glycolaldehyde [13]. In our recent molecular beam mass spectrometric studies of cellulose pyrolysis, we observed a new group of products, which are catalyzed by alkali metals, that corresponded to ions derived from hydroxymethylfurfural and fragments of oligomers containing anhydrosugar and possibly ester linkages [11]. We rationalized this observation as a base-catalyzed process, involving deprotonation by a general base and fragmentation of the resulting anion.

To address these proposed mechanisms, we report here the results of pyrolysis/molecular beam mass spectrometry (MBMS) experiments on cellulose from *Acetobacter* grown on D-(1-^{13}C)-glucose media. Pyrolysis mass spectrometry (Py-MS) has the advantage of nearly complete product analysis, but ambiguities arise due to the nature of the ionization method and the identification of products by their nominal masses [10].

Both the selectively-enriched and unlabeled *Acetobacter* cellulose samples were prepared under identical conditions, and purified in the same way to remove potential metal ion contaminants and to insure that results obtained on all samples could be compared. Results were analyzed statistically to detect changes in the relative intensities of the M + 1 peaks for major ions, and hence determine which products contain the labeled carbon and the extent of incorporation.

2. Experimental

Pyrolysis-molecular beam mass spectrometry.—The MBMS and pyrolysis procedures have been previously described [10], and only a brief description is given here. A sample (5 mg) in a quartz holder is inserted into a helium carrier gas heated to 540 °C. Sample temperature during pyrolysis is typically non-isothermal and cooler than the gas temperature; however, in these comparative and replicated experiments (all experiments were run in triplicate), temperature control is not a major factor. The hot gases are expanded through an orifice into a low pressure chamber to form a molecular beam. Because of the short gas phase residence time (ca. 75 ms) and cooling because of the free-jet expansion, gas-phase pyrolysis is negligible [10]. The molecular beam, collimated through a second expansion, then enters an electron impact ionization source, operated at about 20 eV, to form ions. The mass range of interest (typically 15–300 amu) is scanned each second throughout the complete pyrolysis product evolution. Data are processed by integrating the spectra over the time for the pyrolysis (10 to 90 s, depending on the sample size and temperature), and by subtracting the background signal.

Sample preparation.—The labeled cellulose, selectively-enriched at the C-1 position, was prepared by growing cultures of *Acetobacter xylinum* on a medium that included D-(1-^{13}C)-glucose [14]. Cellulose sheets, or pellicles, were allowed to grow in the medium and then were thoroughly cleaned to remove other biopolymers and metal contamination. The removal of the tenacious cell wall debris was achieved by autoclaving the pellicle in a 1% Alconox solution, followed by extensive washing using ultrapure water (resistivity = 18 MΩ) followed by a 24-hour acid exchange step similar to the procedure of Hshieh and Richards [15] and an additional 24-hour wash with ultrapure water. There was no detectable Na or K present in the control sample analyzed by inductively coupled plasma (ICP) after the clean-up procedure. The extent of ^{13}C enrichment was determined by ^{13}C NMR. D-(1-^{13}C)-Glucose and D-(2-^{13}C)-glucose were obtained from Cambridge Isotope Laboratories, both containing 99 atom% enrichment. Addition of KOH was carried out by wetting the cellulose sample with a given quantity of an aqueous KOH solution such that the amount of KOH added was 0.1% of the sample weight. The sample was then allowed to dry in room temperature air.

Collision-induced dissociation.—Collision-induced dissociation (CID) studies were carried out for several ions using a triple quadrupole mass detector [16]. Pyrolysis product ions were generated in the ion source and the CID daughter mass spectra processed as described above for the basic pyrolysis experiment. In a typical CID experiment, the ion of interest was selected with the first mass filter and allowed to undergo fragmentation in the second RF-only quadrupole by energetic collisions with a target gas (argon) at a pressure of approximately 1×10^{-4} Torr. Collision energies of 15–25 eV in the laboratory frame, calculated as the difference of the ion energy and the collision cell pole-offset voltage, were used. The resulting fragment ions were analyzed by scanning the third quadrupole.

Nuclear magnetic resonance spectroscopy.—The ^{13}C CPMAS NMR spectra were obtained on a Varian XL-200 spectrometer at the carbon resonance frequency of 50.3 MHz. The NMR probe was a Doty Scientific high-speed magic angle spinning probe. For the cross polarization experiments, the initial proton p/2 pulse was 6 ms, corresponding to an RF field of 41.6 kHz. The Hartmann–Hahn match was made at this field strength, whereas the proton decoupling field during the acquisition was ca. 55–60 kHz. The acquisition time was 50 ms with a spectral width of 20 kHz. The pulse repetition time was 2 s. The samples were spun at 4 kHz inside 7 mm cylindrical silicon nitride rotors with Kel-F endcaps.

3. Results and discussion

The pellicles were analyzed by ^{13}C NMR and found to be free of non-cellulosic carbon signals and 14% enriched at the C-1 position. No incorporation of the isotope

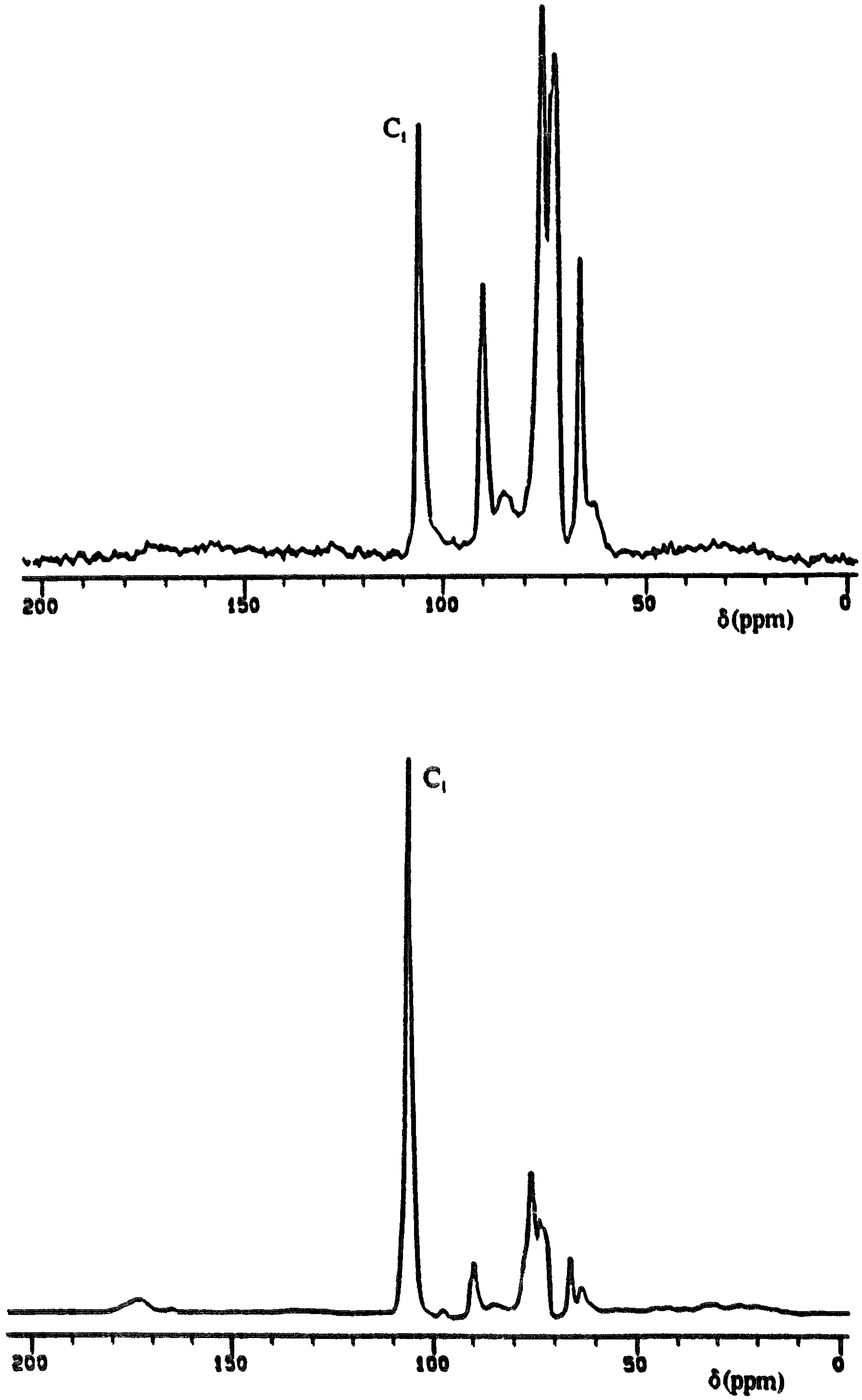


Fig. 1. ^{13}C NMR spectra of regular (top) and (1-^{13}C)-enriched (bottom) *Acetobacter* cellulose. The abscissa is the chemical shift in ppm.

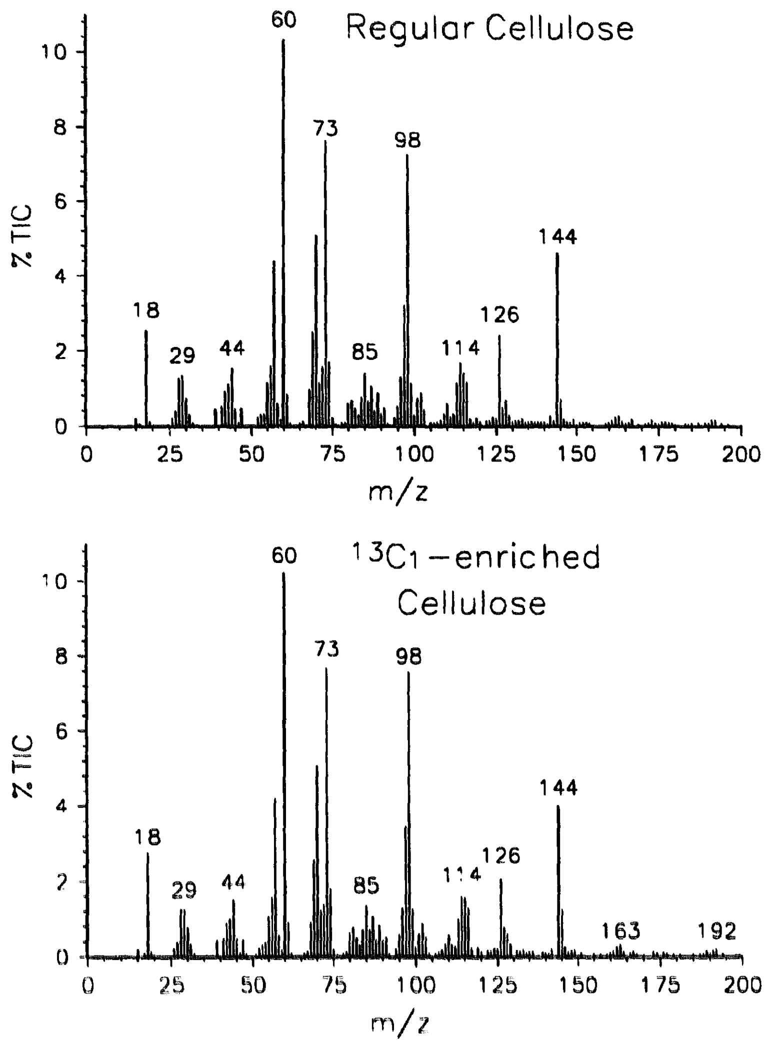


Fig. 2. The average, background-corrected mass spectra of pyrolysis products at 540 °C of regular (top) and (1-^{13}C)-enriched (bottom) *Acetobacter* cellulose.

was observed at other positions. The NMR spectra of unlabeled and labeled cellulose are shown in Fig. 1.

We have previously reported three major groups of products in the pyrolysis mass spectra of cellulose [10]. These groups are: (1) anhydrosugars (m/z 144, 98, 73, and 60), (2) glycolaldehyde (m/z 60, 32, and 31) and related compounds (m/z 42 and 43), and (3) a group of ions that include hydroxymethylfurfural (m/z 126 and 85) and oligomer fragments containing anhydrosugar and ester linkages (m/z 191, 173, 163, 145 and 127; group 3 will be discussed further below). The first two groups are well known in the literature [1–6]. The relative amounts of these three groups are primarily determined by the concentration of alkali metal ions that act as catalysts for the formation of groups 2 and 3.

The difference between the pyrolysis mass spectra of labeled and unlabeled cellulose, shown in Fig. 2, is slight so statistical methods were used to determine significant differences. The ratios of ion peak intensities for some key masses are shown in Table 1.

Table 1
Ratios of key masses in the Py-MBMS of untreated cellulose samples (triplicate analysis)

Ratio	Regular		^{13}C Labeled		Difference
	Values	Average	Values	Average	
m/z 126/144	0.52	0.53	0.45	0.50	−0.03 (±0.08)
	0.54		0.47		
	0.52		0.59		
m/z 60/98	1.42	1.42	1.49	1.36	−0.06 (±0.14)
	1.38		1.37		
	1.45		1.22		
m/z 58/98	0.077	0.077	0.076	0.073	−0.004 (±0.006)
	0.081		0.074		
	0.072		0.069		
m/z 145/144	0.15	0.15	0.29	0.31	0.16 (±0.02)
	0.15		0.30		
	0.16		0.33		
m/z 127/126	0.19	0.19	0.38	0.39	0.20 (±0.04)
	0.21		0.42		
	0.18		0.35		
m/z 111/110	0.42	0.39	0.56	0.53	0.13 (±0.05)
	0.39		0.48		
	0.37		0.54		
m/z 99/98	0.16	0.16	0.17	0.17	0.01 (±0.01)
	0.16		0.16		
	0.15		0.17		
m/z 61/60	0.076	0.081	0.083	0.089	0.008 (±0.008)
	0.088		0.092		
	0.078		0.091		
m/z 45/44	0.30	0.30	0.28	0.31	0.01 (±0.03)
	0.29		0.33		
	0.30		0.31		
m/z 192/191	0.89	0.88	1.24	1.21	0.33 (±0.09)
	0.80		1.19		
	0.95		1.21		

The ratio of m/z 126/144 (both m/z 126 and 144 are six-carbon species) is a sensitive indicator of the relative amounts of product groups 3 and 1, respectively. Two other ratios, m/z 60/98 and m/z 58/98, which may also show variations with pyrolysis conditions and the alkali metal presence, are also included in Table 1. These ions represent several other major peaks in the pyrolysis mass spectra of cellulose. The

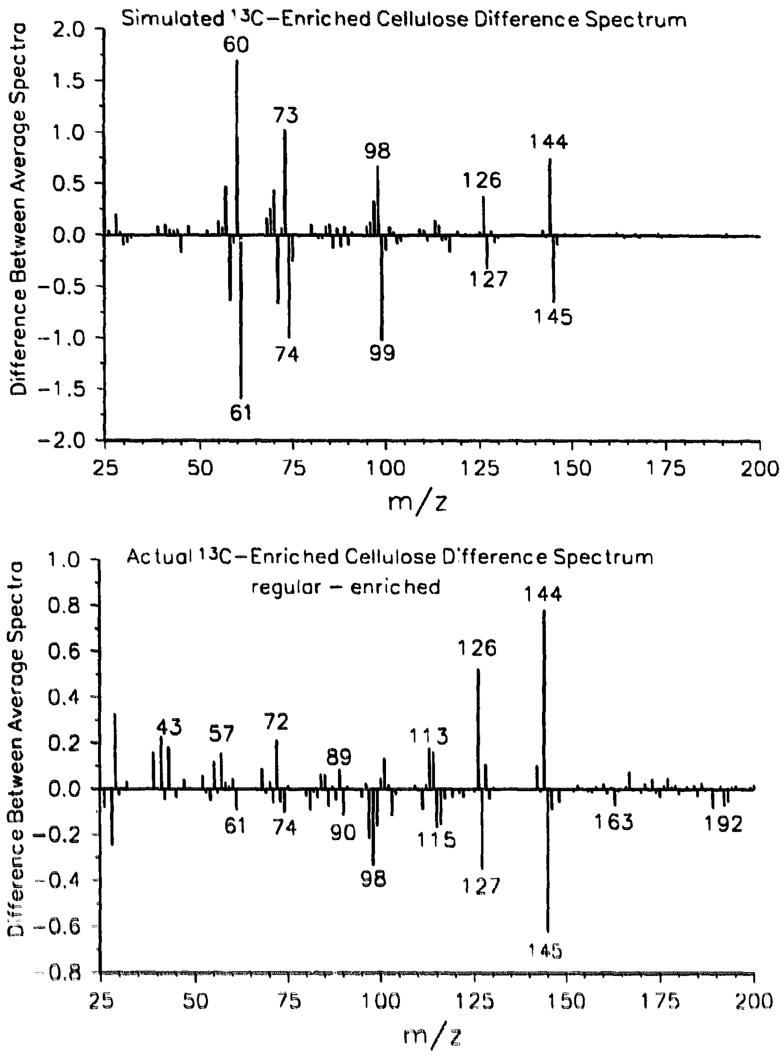


Fig. 3. The simulated and actual difference spectra between regular and 14% (1-^{13}C)-enriched cellulose.

m/z 60 peak may be either a fragment ion of levoglucosan or the molecular ion of acetic acid and glycolaldehyde; m/z 58 is assigned as acetone (mainly observed in cellulose pyrolysis with alkali metal present); furfuryl alcohol is the likely product at m/z 98. The data in Table 1 lead to the conclusion that there is no significant difference between the two samples in the relative amounts of these groups. Therefore, the differences in m/z 145/144 and m/z 127/126 are assumed to be due to the enrichment at the C-1 position. These results indicate that the ^{13}C-label is present in six-carbon species, as judged by the differences in the m/z 145/144, m/z 127/126, and m/z 111/110 ratios of 0.16, 0.20, and 0.13, respectively, and they correspond, within experimental error, with the NMR-determined value of 14% enrichment at the C-1 position. The ratios of m/z 99/98, m/z 61/60, and m/z 45/44 show no enrichment at m/z 98, 60, and 44, respectively, and we conclude that the corresponding products of these ions are not formed from the C-1 position in the cellulose anhydroglucose units under these pyrolysis conditions (or ion source fragmentation

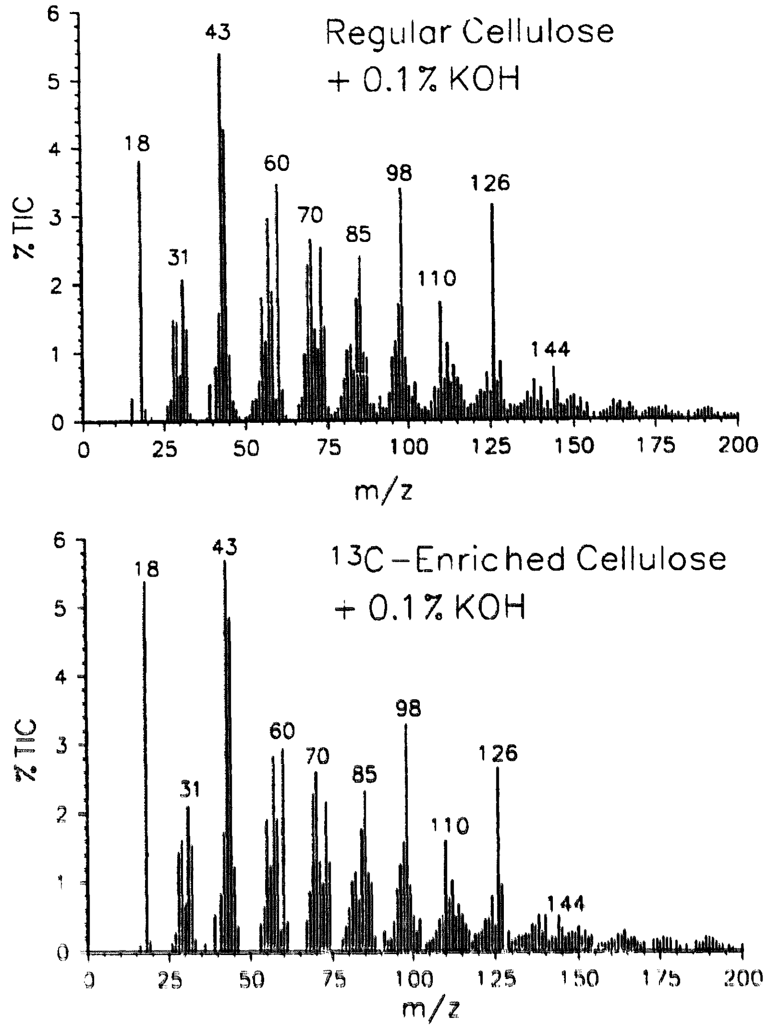


Fig. 4. The average, background-corrected mass spectra of pyrolysis products at 540 °C of regular (top) and (1-^{13}C)-enriched (bottom) *Acetobacter* cellulose treated with 0.1% KOH.

conditions). The *m/z* 192/191 ratio indicates an increase of 0.33 in the labeled sample, which suggests the presence of two C-1 carbons in this species. This result will be discussed further.

To assist interpretation, a simulated, enriched spectrum, based on 14% ^{13}C enrichment at every mass in the pyrolysis spectrum of the regular cellulose, was calculated and the two spectra were compared by subtraction. Although there are varying numbers of carbons in each ion, this assumption is probably the best approach since most of the ions in the pyrolysis mass spectra of cellulose contain no more than one C_6 unit, i.e., at most one carbon being ^{13}C-enriched. The simulated difference spectrum is shown in Fig. 3 (top), where masses that are higher in the simulated ^{13}C-labeled sample have negative values. This simulated difference spectrum serves as a model to evaluate the authentic results reported below.

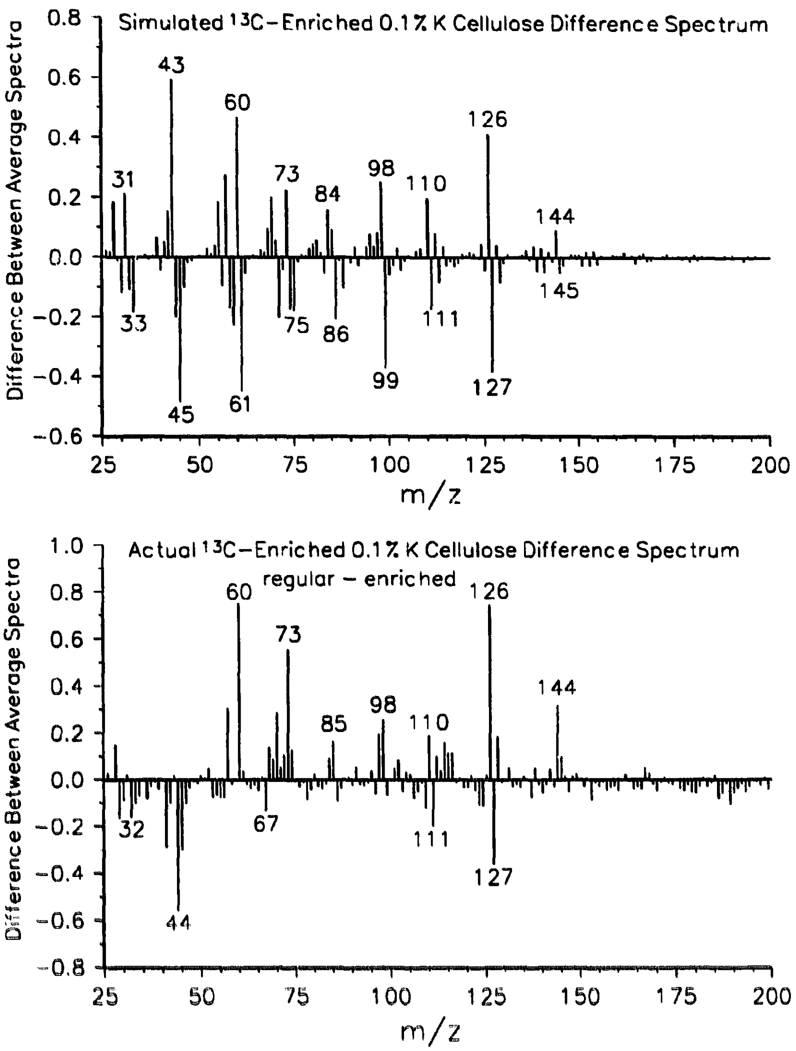


Fig. 5. The simulated and actual difference spectra between the alkali-treated regular and 14% (1-^{13}C)-enriched cellulose.

The authentic ^{13}C-labeled cellulose pyrolysis difference spectrum is shown in Fig. 3 (bottom). The distributions in the simulated and actual difference spectra around *m/z* 126 and 144 are quite similar. However, there are no significant low mass products that show ^{13}C enrichment in a distribution similar to that in the simulated difference spectrum. The cluster around *m/z* 98 is also strikingly different from that in the simulated difference spectrum. This result implies a more complex condition for this cluster than assumed in the simulated data, such as multiple sources for these ions and some that may not contain the C-1 position. It is also possible that a given pyrolysis product may come from more than one position in the anhydroglucose monomer.

For these clean cellulose samples, it is likely that *m/z* 60 is an EI fragment ion of levoglucosan and not of glycolaldehyde [10]. To force the distribution of pyrolysis products toward the aldehyde product set, samples of the *Acetobacter* cellulose were treated with 0.1% KOH and analyzed similarly to the samples described above. The

Table 2
Ratios of key masses in the Py-MBMS of cellulose samples treated with 0.1% KOH (triplicate analysis)

Ratio	Regular		^{13}C-Labeled		Difference
	Values	Average	Values	Average	
m/z 126/144	3.9	4.2	6.6	5.5	1.4 (±1.1)
	4.4		5.5		
	4.3		4.5		
m/z 60/98	1.25	1.02	0.71	0.87	−0.15 (±0.25)
	0.91		0.96		
	0.89		0.94		
m/z 58/98	0.54	0.54	0.61	0.59	0.05 (±0.05)
	0.52		0.61		
	0.57		0.54		
m/z 145/144	0.47	0.55	0.74	0.69	0.14 (±0.08)
	0.57		0.69		
	0.60		0.65		
m/z 127/126	0.17	0.18	0.36	0.37	0.19 (±0.03)
	0.18		0.34		
	0.18		0.40		
m/z 111/110	0.36	0.33	0.45	0.48	0.16 (±0.05)
	0.30		0.52		
	0.33		0.48		
m/z 99/98	0.27	0.26	0.33	0.30	0.04 (±0.03)
	0.26		0.28		
	0.24		0.29		
m/z 61/60	0.12	0.12	0.12	0.14	0.02 (±0.02)
	0.10		0.15		
	0.13		0.14		
m/z 59/58	0.13	0.16	0.16	0.16	0.00 (±0.03)
	0.16		0.16		
	0.18		0.15		
m/z 192/191	0.98	0.88	0.76	0.79	−0.09 (±0.11)
	0.87		0.79		
	0.78		0.83		

resulting pyrolysis mass spectra are shown in Fig. 4 and the difference spectra calculated for the treated samples, by the method stated above, are displayed in Fig. 5. Ion intensity ratios for some major products are listed in Table 2. The reproducibility is slightly worse in the pyrolysis of these KOH-treated samples due to the sample preparation step. However, there is again no clear trend for the low-molecular-weight ions. Only m/z

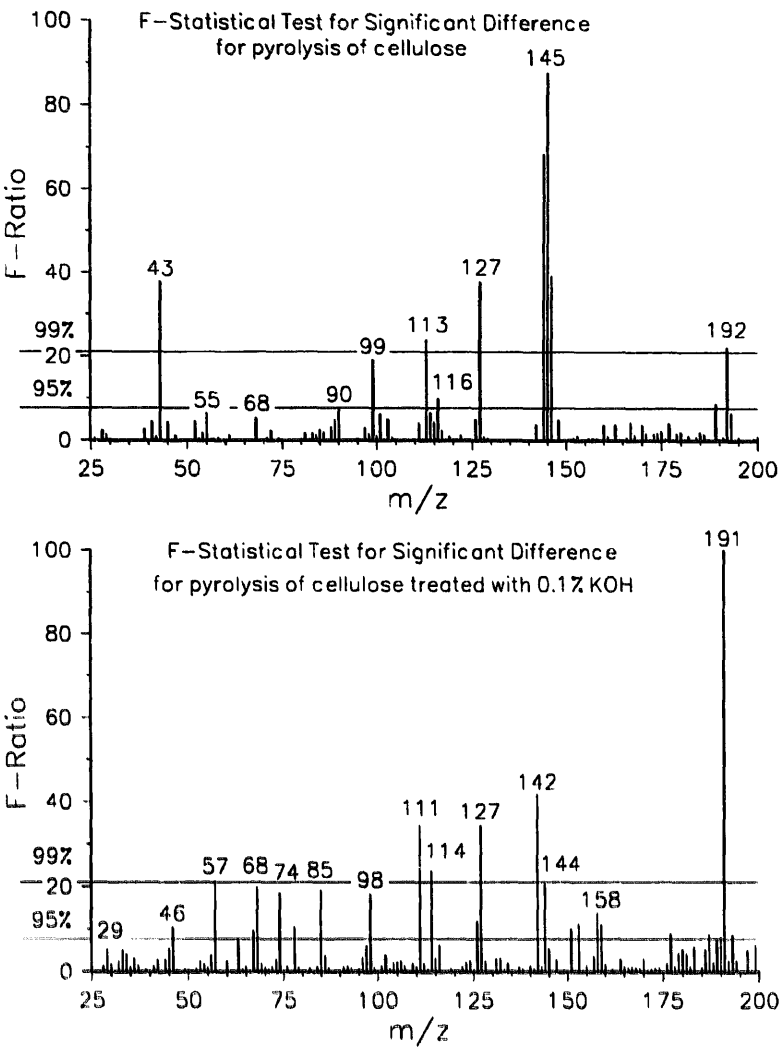


Fig. 6. Statistical significance for the comparisons in Fig. 3 (top) and Fig. 5 (bottom). Note the 95% and 99% confidence levels shown and see text for explanation.

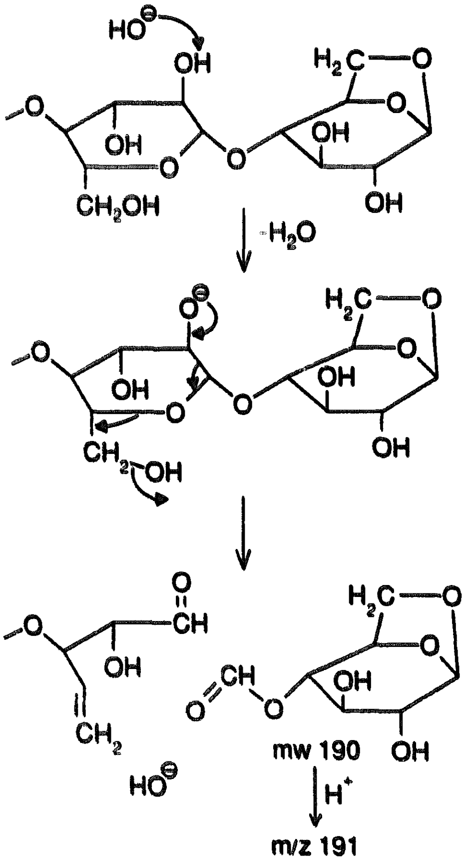
126 and 110 show significant enrichment. These data indicate that the *m/z* 60 products that are present under alkali-catalyzed conditions are not formed from the C-1 position in cellulose, and glycolaldehyde and/or acetic acid must come mainly from the C-2 to C-6 positions. This conclusion will be discussed later in relationship to ^{13}C-labeled glucose.

An important consideration in viewing these difference spectra is the statistical significance of the differences. An analysis of variance (ANOVA) was performed on the triplicate runs for the two samples. The results are presented as an F ratio spectrum in Fig. 6, where the F ratio for each mass is plotted vs. its *m/z* value. The F ratio is a statistical parameter used to estimate the probability of significant differences between replicated samples, and is calculated by comparing inner and outer variations for three replicate experiments of each sample. In these cases, an F ratio of 7.71 indicates 95% confidence that the measured difference is significant and an F ratio of 21.2 implies 99%

confidence. This analysis confirms that no low mass products result from the enriched C-1 position. Note that in the *m/z* 98 cluster, only *m/z* 99 is significantly different. This is somewhat intriguing since we failed to see any significant change in the ratio of *m/z* 99/98 in the pyrolysis mass spectra of unlabeled and the ^{13}C-enriched cellulose. This result implies that one of the sources contributing to the *m/z* 98 peak may contain C-1, although we do not know how large the contribution is.

One of the more significant pairs of masses shown in Fig. 6 is *m/z* 191 and 192, despite the variability shown in Table 1 and the low intensity of this peak. They are of great interest since it is statistically significant (see Fig. 6, and notice the large F ratios which correspond to greater than the 99% confidence level) and correspond to twice the enrichment of 14% observed for *m/z* 144/145, 126/127 and 111/110 (Tables 1 and 2). This is evidence that the *m/z* 191 ion contains two C-1 carbons. Furthermore, it is a higher *m/z* than the anhydrosugar (MW = 162), and it is an odd mass ion, indicating either a protonated *m/z* 190 or a fragment ion of a higher mass, such as *m/z* 192 or higher. The peaks at *m/z* 173, 163 and 145 in the pyrolysis mass spectra of cellulose samples are correlated with the intensity of *m/z* 191. These ions are associated with the third group of pyrolysis products mentioned above [10].

We have performed CID experiments on these ions to learn more about their structure. The species at *m/z* 191 gives rise to the following daughter ions (shown in



Scheme 1.

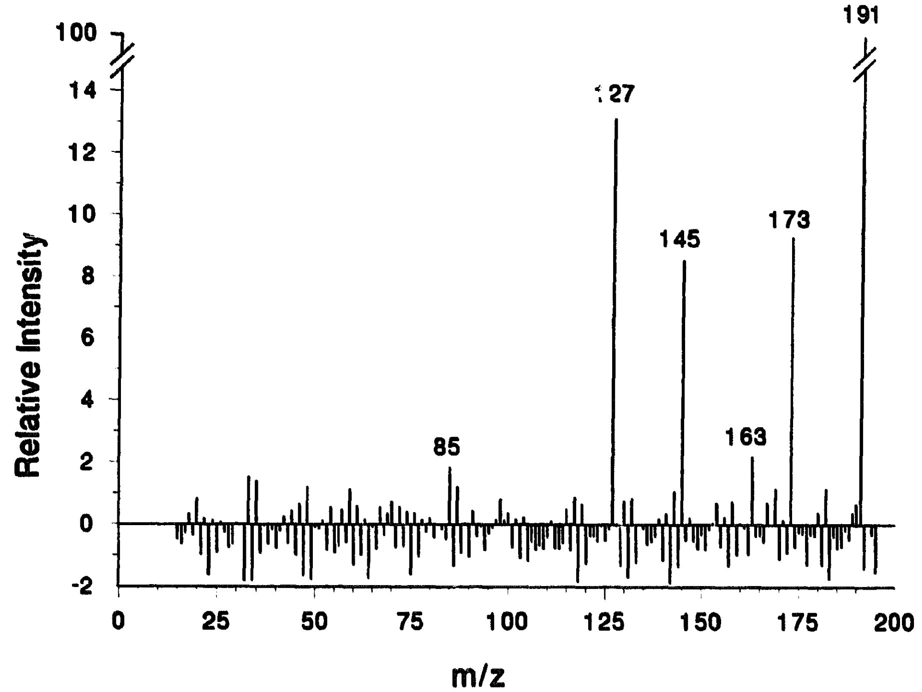


Fig. 7. CID daughter mass speectrum of m/z 191 during the pyrolysis of avicel cellulose (PH 102). See text for CID conditions and a discussion of this spectrum.

Fig. 7): m/z 173 ($-H_2O$), m/z 163 (−CO), m/z 145 ($-HCO_2H$), and m/z 127 ($-H_2O-HCO_2H$). A plausible hypothesis is that an adjacent C-1 is attached to an anhydroglucose unit through an ester linkage. The series of daughter ions of m/z 191, at m/z 163, 145 and 127, resemble the dehydration series from the EI fragment ions of levoglucosan at m/z 162, 144 and 126, implying that the parent of m/z 191 may be an anhydrosugar derivative. The peak at m/z 163 may be an EI fragment ion of the same species that produces m/z 191 and also forms daughter ions at m/z 145 and 127. Arisz et al. have characterized oligomers and sugar ring cleavage products in cellulose pyrolysis and found a series of ions using soft ionization techniques [17]. It is quite possible that the m/z 191 and associated peaks are related to these same oligomer fragments. An alternative explanation for m/z 191 and associated masses is that it is formed from post-pyrolysis reactions between glycolaldehyde and levoglucosan, either with each other or with the remaining cellulose chain. To test this hypothesis, cellulose was pyrolyzed in the presence of both compounds and no effect on m/z 191 was observed. Therefore, m/z 191 is assumed to result from a primary product of cellulose pyrolysis.

We therefore propose the following mechanism (Scheme 1) for the formation of m/z 191 series of ions in the pyrolysis mass spectra of cellulose. It begins with a deprotonation by a general base (HO^- is shown here as an example) of the hydroxyl group at the C-2 position on the glucose unit next to the levoglucosan end group. The resulting anion undergoes fragmentation to produce the levoglucosan formate ester

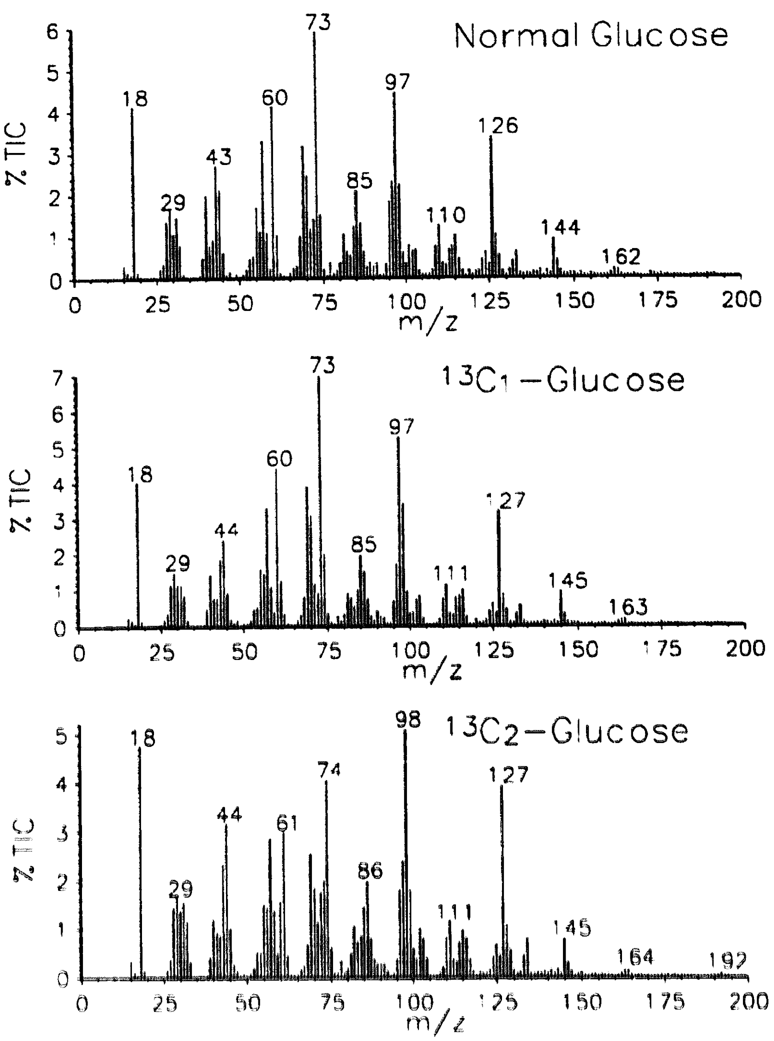


Fig. 8. The average, background-corrected spectra of pyrolysis products at 540 °C of normal glucose, (1-^{13}C)-glucose, and (2-^{13}C)-glucose.

(MW = 190), which is then protonated to give *m/z* 191 during ionization of the molecular beam. Alternatively, this *m/z* 191 ion can result from fragmentation during the ionization of larger species such as 4-hydroxyethyl-1,6-anhydroglucopyranose (MW = 222, by losing HOCH$_2$). This species belongs to the series of (anhydro)-oligosaccharides with attached ring-cleavage fragments, which have been previously reported by Arisz et al. using in-source pyrolysis chemical ionization mass spectrometry [17]. Electrocyclic mechanisms leading to the formation of these species with MW = 190 and 222 can not be eliminated from the results presented here, but the catalytic effect of alkali metals seems to favor the pathway proposed in Scheme 1.

It is well known that there are significant differences between the pyrolysis of glucose and cellulose [1–4]. However, the pyrolysis mass spectra are similar enough to allow some extrapolation, and working with labeled glucose samples that are 99% ^{13}C-labeled at C-1 and C-2 allow more direct interpretation of the results. The pyrolysis

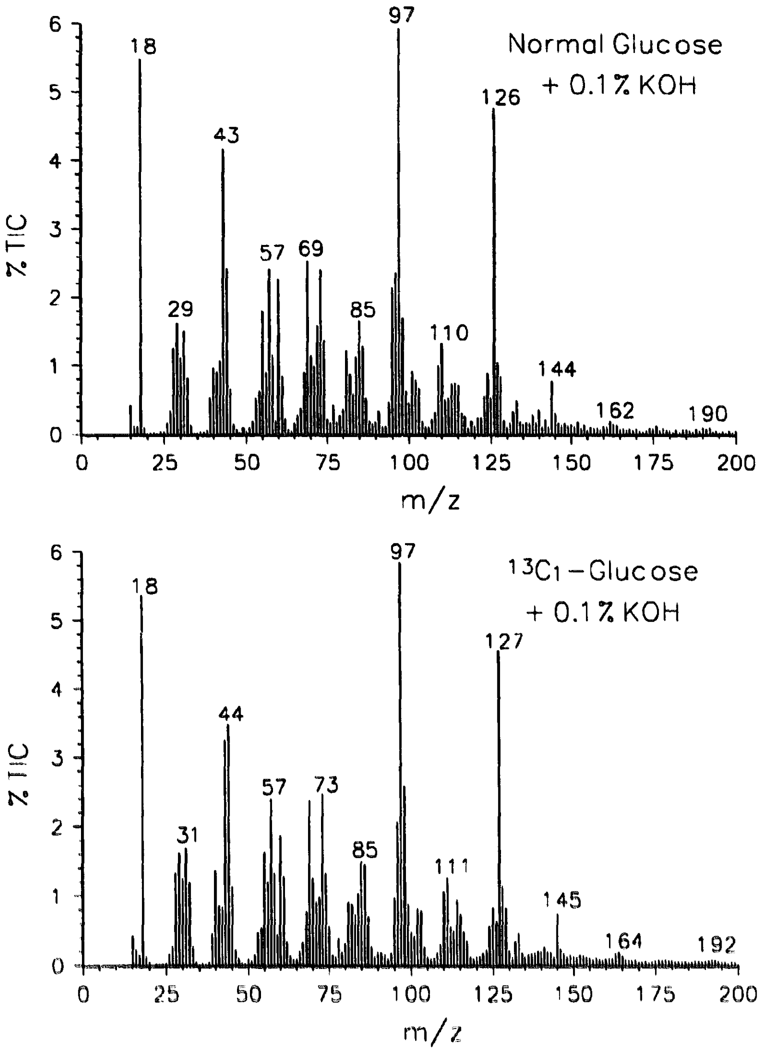


Fig. 9. The average, background-corrected spectra of pyrolysis products at 540 °C of normal glucose and (1-^{13}C)-glucose treated with 0.1% KOH.

mass spectra for regular, (1-^{13}C)-, and (2-^{13}C)-glucose are shown in Fig. 8. The main differences between the spectra of glucose and cellulose pyrolysis products are a lower relative abundance of levoglucosan ions (*m*/*z* 162 and fragment ion at *m*/*z* 144) and a higher relative abundance of 5-hydroxymethylfurfural ions (*m*/*z* 126 and fragment ion at *m*/*z* 97). The same trends noted for the labeled cellulose are present: C_6 species show a switch to the M + 1 peaks as expected, but again minimal M + 1 enrichment is observed at the low masses. This contrasts with the (2-^{13}C)-glucose results which show major enrichment at the M + 1 peak for the low masses including *m*/*z* 60 and 32. The normal glucose and (1-^{13}C)-labeled glucose was treated with 0.1% KOH to force the glycolaldehyde pathway. The spectra of pyrolysis products are shown in Fig. 9. Note that glucose is not as sensitive to this level of addition as cellulose. The results are similar to those for cellulose showing only small increases in the *m*/*z* 61/60 ratio.

4. Summary and conclusions

The use of labeled feedstocks has allowed some insight into the pathways of cellulose pyrolysis regarding the reaction of the C-1 position. Results of the pyrolysis of *Acetobacter* cellulose containing 14% ^{13}C enrichment at C-1, and D-(1-^{13}C)-glucose, indicate only a small contribution to glycolaldehyde and other *m/z* 60 ions (i.e., a fragment ion of levoglucosan). Although C-1 is present to only a minor degree in the low-molecular-weight products, it appears to be a critical factor in the formation of anhydrosugars with ester side chains, which are believed to give *m/z* 191. By comparison, the C-2 position of glucose appears in all major low-molecular-weight ions. Future work will include pyrolysis of cellulose samples labeled with ^{13}C at other positions that is currently being prepared using D-(2-^{13}C)- and (6-^{13}C)-glucose. However, we have found that D-(2-^{13}C)-glucose produced a cellulose sample with partial ^{13}C enrichment at 2-, 3-, and 4-positions. We are also carrying out detailed CID studies of enhanced masses to determine the exact position of enrichment.

On the other hand, mass spectrometric studies of the ^{13}C-labeled glucose samples, and in particular, CID experiments on ^{13}C-containing molecular ions and major fragment/product ions from ionization or pyrolysis, will provide useful information pertaining to the chemistry involved in the pyrolysis and ion fragmentation for glucose and its major pyrolysis products, e.g., levoglucosan. Results of these experiments will be published in the near future.

5. Note added in proof

During the preparation of this paper, which is based on work completed several years ago [18], we became aware of some excellent work by Ponder and Richards [19] on the pyrolysis of ^{13}C-labeled glucans. From their ^{13}C NMR and GLC/MS results, it was concluded that several different mechanisms are involved in the formation of each of the low-molecular-weight products (glycolaldehyde, acetol, acetic acid, and formic acid) from the pyrolysis of glucans, but only a few mechanisms predominate. Glycolaldehyde mainly derives from C-1–C-2 of glucans, with minor contribution from C-5–C6. The methyl group of acetic acid originates mostly from C-6 and C-1. We have come to similar conclusions from results obtained in our CID studies of the pyrolysis of ^{13}C-labeled cellulose and glucose [20].

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