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# Pyrolysis of some $^{13}$C-labeled glucans: A mechanistic study †

Glenn R. Ponder and Geoffrey N. Richards *

*Wood Chemistry Laboratory, University of Montana, Missoula, Montana 59812 (USA)*

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## ABSTRACT

An isotopic labeling study has been conducted to investigate the chemical mechanisms involved in the formation of certain pyrolysis products of glucans, specifically glycolaldehyde (GA), acetol (hydroxypropanone), acetic acid, and formic acid, which are the major non-aqueous components of the distillate fraction (−60°C condensate) of the pyrolyzate. $^{13}$C labels at C-1, C-2, and C-6 of the glucose rings in synthetic glucans were used to reveal the origins of these compounds. In general, the results show that each compound is formed by several different mechanisms, but suggest that only a few mechanisms predominate in each case. Glycolaldehyde derives predominantly from the C-1–C-2 segment of the glucose monomers, with C-5–C-6 also contributing significantly. Evidence is presented supporting heterolytic mechanism which require a reducing end-group and base catalysis. Acetol derives mostly from three contiguous carbons that include a terminal carbon (C-1 or C-6), most often C-6 and most often appearing as the methyl carbon in the acetol. Acetic acid also arises most often from terminal carbons, the C-5–C-6 segment being the major source, with the methyl carbon usually deriving from C-1 or C-6. About half of the formic acid produced arises from C-1. Mechanisms derived from the chemistry of alkaline degradation and involving acylformylcarbinol intermediates are proposed.

## INTRODUCTION

Prior studies of cellulose pyrolysis have shown that removal of indigenous inorganic impurities (specifically, metal ions) results in a large increase in yield of anhydro sugar accompanied by a decrease in products characteristic of base-catalyzed dehydration, rearrangement, and/or fragmentation. Moreover, the pyrolytic formation of the latter compounds from cellulose is known to be increased by prior addition of ionic impurities, especially basic impurities. Recent work has shown that such pyrolytic behavior is common to all glucans[1]. Formation of the same compounds in about the same relative proportions from all of the glucans studied suggests that the nature of the glycosidic linkages in a given glucan has little effect upon major reaction-pathways.

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* Corresponding author.

The work herein is an isotopic labeling study designed to determine the origins of the major one-, two-, and three-carbon compounds formed in glucan pyrolysis. The substrate used in the study is a randomly linked glucan, synthesized as described previously[2]. Implicit in this study is the assumption that the types and orientations of the glucosidic linkages are not important in this context of pyrolysis. The origins of four compounds are considered: glycolaldehyde (GA), acetol (hydroxypropanone), acetic acid, and formic acid. Previous speculations on pyrolytic mechanisms leading to these compounds form cellulose are now briefly considered. They will be reconsidered in light of the labeling results.

The idea that 1,6-anhydro-β-D-glucopyranose (levoglucosan, LG) serves as an intermediate in the formation of smaller compounds has been a popular one in the literature[3,4]. Berkowitz-Mattuck et al.[5] proposed a mechanism involving fragmentation of LG to yield a 5-deoxy-4-pentulose intermediate which subsequently undergoes homolytic fragmentation to give GA from the C-2–C-3 segment of glucose or reverse aldol reaction to give acetol from the C-3–C-4–C-5 segment. Another example, often cited, of the LG-as-intermediate-idea was proposed by Shafizadeh and Lai[6], and involves LG hydrating to glucose, the aldehyde form of which then undergoes reverse aldol reaction to yield GA from C-1–C-2. These authors further suggested that the remaining tetrose can undergo dehydration to yield 2-hydroxy-3-oxobutanal (**1**) and decarbonylation to yield acetol from C-4–C-5–C-6. This concept of a preferential decomposition of the monomer unit of cellulose to a two-carbon fragment and a four-carbon fragment is one which is seen in several of the proposed mechanisms. Of course, the glucose unit to which these concepts can be applied need not necessarily arise via LG.

A dehydration product of glucose, 3-deoxy-D-*erythro*-hexosulose (**2**) also has been suggested as an intermediate leading to smaller compounds in glucan pyrolysis[6]. Shafizadeh and Lai[7] suggested that it undergoes reverse aldol reaction to yield glyceraldehyde from C-4–C-5–C-6; the glyceraldehyde then disproportionates to give formaldehyde form C-4 and GA from C-5–C-6. Byrne et al.[8] suggested that GA arises from C-1–C-2 by heterolytic fragmentation of a glucopyranosyl cation end-group. This is a variation on the concept of decomposition to two-carbon and four-carbon fragments. Yet another variation on this theme is an anionic mechanism suggested by Evans and Milne[9] as the "alkali-metal-catalyzed pathway" for cellulose. The mechanism involves deprotonation and ring opening of a glucopyranose reducing end-group, and fragmentation of the resulting anion to give GA from C-5–C-6.

An electrocyclic mechanism leading to GA from C-5–C-6 has been suggested[10]. In this mechanism an in-chain unit undergoes dehydration followed by retro-Diels–Alder reaction. Another electrocyclic mechanism leading to GA from C-5–C-6 has been proposed by Lomax et al.[11]. This involves a concerted fragmentation of an in-chain glucose ring of cellulose into three two-carbon fragments. The two remaining two-carbon fragments might stay attached to the neighboring glucose residues, possibly leading to free glucose molecules with acetaldehyde fragments

attached at O-1 or O-4. Lomax et al. did in fact identify such derivatives in the permethylated pyrolyzate of cellulose.

The idea of concerted fragmentation of the glucose ring to form three two-carbon fragments has been applied to free glucose itself by Kang et al.[12]. This results in three molecules of GA, two of them initially in the enol form. These authors further suggest that some of the GA dehydrates under pyrolytic conditions to form ketene, which then rehydrates to form acetic acid. In support of this, Kang et al. detected ketene in the pyrolyzates of several monosaccharides, and ketene has also been reported as a component in the pyrolyzate of amylose[13].

The pyrolytic formation of formic acid may be regarded as analogous to its formation under conditions of alkaline degradation[10]. It has long been known that alkaline degradation of cellulose gives high yields of formic acid[14], and Koetz and Neukom[15] have proposed a mechanism for this reaction involving a peeling reaction from the reducing end-group. Base-catalyzed carbonyl migration and $\beta$-alkoxycarbonyl elimination result in a 4-deoxy-2,3-hexodiulose intermediate, which has been identified in the alkaline digests of maltose[16]. Another carbonyl migration gives a 4-deoxy-3-hexosulose intermediate, a transformation that competes with isosaccharinic acid formation[17,18]. Hydrolysis then yields formic acid from C-1. Support for the idea that C-1 is the source of formic acid in pyrolysis (at least of glucose) is provided by the work of Houminer and Patai[19]. These workers studied the pyrolysis of $^{14}$C-labeled glucose and found that formic acid originates predominantly from C-1. Support for the idea that pyrolytic formation of formic acid is base-catalyzed is provided by the fact that the highest yield of formic acid (7.4%)[20] is obtained from cellulose treated with sodium hydroxide. In fact, base-catalysis appears to play a role in the pyrolytic formation of all four of the compounds under consideration, and other parallels between pyrolysis and alkaline degradation will be considered.

## RESULTS AND DISCUSSION

The starting material for synthesizing the labeled glucans was $^{13}$C-labeled glucose with the label at C-1, C-2, or C-6. After five-fold dilution with unlabeled glucose and conversion into methyl $\alpha,\beta$-glucopyranoside ($\alpha\beta$-MeG), this was thermally polymerized as described earlier to produce a randomly linked glucan (MeGpol)[2]. These polymer products will be referred to as 1-$^{13}$C-MeGpol, 2-$^{13}$C-MeGpol, and 6-$^{13}$C-MeGpol, respectively. A preliminary vacuum pyrolysis of untreated 1-$^{13}$C-MeGpol, followed by $^{13}$C NMR analysis of the room-temperature condensate (i.e., the tar fraction, which was predominantly LG) confirmed that the label in LG had remained at its original position throughout the synthesis and pyrolysis.

Each of the three labeled glucans was treated with 1% (w/w) NaCl, by freeze-drying from concentrated aqueous solution, in order to optimize pyrolytic yield of the carbonyl compounds and carboxylic acids of interest. Vacuum pyroly-

ses (1.5 mm Hg, 300°C for 30 min) were conducted on a 0.25-g scale, larger amounts than this being impractical due to foaming of the polymer melt during pyrolysis. The "distillate" fraction of the pyrolyzate (−60°C condensate, after removal of tar fraction) was analyzed by NMR or by GLC–MS to determine the distribution of label in the pyrolysis products. Distillate fractions were prepared for analysis in one of three ways, depending on the analytical method to be used and the products to be analyzed. For NMR analysis of GA and acetol, $D_2O$ containing an internal standard was added to the distillate fraction. For NMR analysis of acetic and formic acids, distillate fractions from two to four pyrolyses were combined, neutralized, and evaporated to dryness before addition of $D_2O$ and internal standard. For GLC-MS analysis of acetol and the acids, the aqueous solution was injected directly onto GLC capillary column. GA did not behave satisfactorily in GLC and was not analyzed by this method.

The NMR analysis of isotopic enrichment of each carbon in each of the four compounds of interest is described in the Experimental section. Two or three pyrolysis experiments were conducted for each label position to ascertain reproducibility. Fig. 1 shows a typical $^{13}C$ NMR spectrum of the distillate fraction from pyrolysis of 1-$^{13}C$-MeGpol. Table I gives the percent of carbons derived from the label for the GA carbons and for the terminal carbons of acetol. Results from three separate pyrolyses of 1-$^{13}C$-MeGpol, and from two pyrolyses each of the other two polymers, are given. Standard deviations are calculated from appropriate propagation of error formulae[21] assuming a 5% coefficient of variation for the area ratio measurements taken from the $^{13}C$ NMR spectra.

Table II gives the percent of carbons derived from the labeled position for the methyl carbon of acetic acid and for the formic acid carbon. Distillate fractions from four pyrolyses of 1-$^{13}C$-MeGpol were combined, and distillate fractions from two pyrolyses each of the other two polymers were combined, to obtain the results.

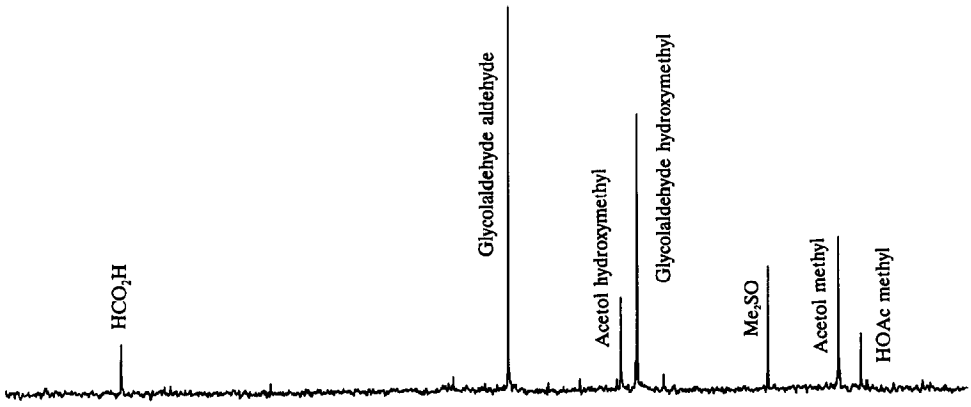



Fig. 1. $^{13}C$ NMR spectrum of distillate fraction from pyrolysis of 1-$^{13}C$-MeGpol.

TABLE I

Glycolaldehyde and acetol, percent of carbons from labeled position

| Label position | Glycolaldehyde | | Acetol | |
|---|---|---|---|---|
| | $CH_2OH$ | CHO | $CH_3$ | $CH_2OH$ |
| 1 | 17 ±1 | 24 ±2 | 20 ±1 | 7 ±1 |
| | 19 ±1 | 21 ±2 | 21 ±2 | 7 ±1 |
| | 17 ±1 | 20 ±1 | 20 ±1 | 6 ±1 |
| 2 | 19 ±1 | 22 ±2 | 6 ±1 | 17 ±1 |
| | 24 ±2 | 27 ±2 | 4 ±1 | 15 ±1 |
| 6 | 13 ±1 | 13 ±1 | 48 ±3 | 3 ±1 |
| | 14 ±1 | 14 ±1 | 55 ±3 | 7 ±1 |
| 0 [a] | −0.1±0.3 | 0.2±0.3 | −0.1±0.3 | 0.0±0.3 |

[a] Unlabeled MeGpol.

For GLC–MS analyses, the degree of isotopic enrichment of molecular ions and certain fragment ions seen in the mass spectra of three pyrolysis products was determined by comparing the ratio M/(M + 1) for the labeled case to the corresponding ratio for the unlabeled case. Five masses, and their corresponding M + 1 values, were measured. These were: from formic acid, the molecular ion; from acetic acid, $(CO_2H)^+$ and the molecular ion; and from acetol, $(CH_2OH)^+$ and $(COCH_3)^+$. Enrichments of the methyl carbon in acetic acid and of the methyl carbon in acetol were calculated as described in the Experimental section.

For each of the five masses considered, three to five repeat injections of the distillates onto the GLC column were made, followed by mass spectral calculations. Table III gives the results of these analyses. Three distillate fractions, each from one pyrolysis of one of the three labeled polymers, were used to obtain this data. Thus, for each label position, the values in Table III are replicate measurements from the same pyrolysis experiment, the differences being due to instrumentation variables. (In contrast, the NMR data in Table I derives from separate pyrolyses, so that differences between those values are due to pyrolysis variables as well.) Table IV summarizes all of the labeling results and compares results from the two analytical methods. Except of the NMR-derived data for the acids, the

TABLE II

HOAc and $HCO_2H$, percent of carbons from labeled position

| Label position | Acetic acid $CH_3$ | Formic acid |
|---|---|---|
| 1 | 27 ±2 | 47 ±4 |
| 2 | 2 ±1 | 6 ±1 |
| 6 | 45 ±6 | 3 ±1 |
| 0 [a] | −0.3±0.7 | −0.6±0.5 |

[a] Unlabeled MeGpol

TABLE III

GLC–MS results, percent of carbons from labeled position

| Label position | Formic acid | Acetic acid | | Acetol | |
|---|---|---|---|---|---|
| | | $CH_3$ | $CO_2H$ | $CH_3$ | $CH_2OH$ |
| 1 | 41 | 24 | 6 | 22 | 10 |
| | 45 | 23 | 5 | 23 | 9 |
| | 41 | 25 | 5 | 21 | 9 |
| 2 | 4 | 4 | 32 | 7 | 15 |
| | 5 | 6 | 32 | 9 | 16 |
| | 4 | 6 | 30 | 5 | 15 |
| 6 | 4 | 42 | 3 | 48 | 5 |
| | 3 | 40 | 3 | 46 | 4 |
| | 4 | 42 | 4 | 46 | 6 |

values shown in Table IV are averages of the replicate measurements of Table III and of the results of repeat pyrolyses in Table I.

It is apparent from the results shown in Table I–IV that the two analytical methods confirm each other, and that the distribution of label is reasonably consistent from one pyrolysis to the next. Significantly, every carbon analyzed shows isotopic enrichment to some degree in every case, indicating that the glucose ring can fragment in a variety of different ways, many of them leading to one or more of the four compounds under consideration. Previous speculations[22] that each product may be formed by several different mechanisms are thus confirmed.

The results shown in Table IV for the C-1 labeled case indicate that ~ 40% of the GA originates from C-1–C-2. Results for the C-2 labeled case show that

TABLE IV

Comparison of methods, percent of carbons from labeled position [a]

| Label position | 1 | | 2 | | 6 | |
|---|---|---|---|---|---|---|
| | NMR | MS | NMR | MS | NMR | MS |
| GA | | | | | | |
| CHO | 22 | nd | 24 | nd | 14 | nd |
| $CH_2OH$ | 18 | nd | 21 | nd | 13 | nd |
| Acetol | | | | | | |
| $CH_3$ | 20 | 22 | 5 | 7 | 52 | 47 |
| $CH_2OH$ | 7 | 10 | 16 | 16 | 5 | 5 |
| HOAc | | | | | | |
| $CH_3$ | 27 | 24 | 2 | 6 | 45 | 42 |
| $CO_2H$ | nd | 5 | nd | 31 | nd | 3 |
| $HCO_2H$ | 47 | 42 | 6 | 4 | 3 | 4 |

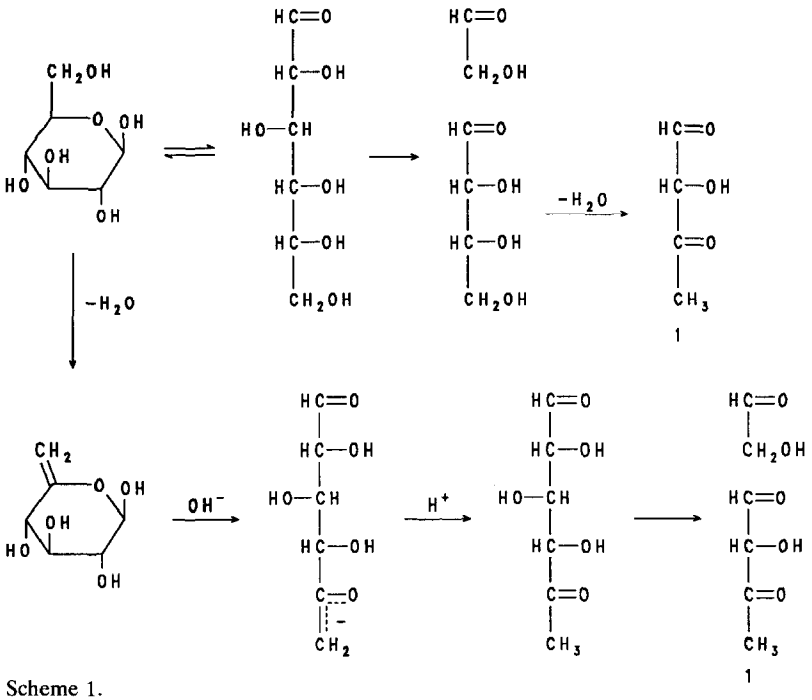
[a] nd, not determined.

~ 45% of the GA originates from C-1–C-2 and/or from C-2–C-3. Because these values are approximately equal, it is concluded that little or no GA arises from C-2–C-3. The mechanism proposed by Berkowitz-Mattuck et al.[5] must therefore be excluded as a possible major pathway (it is also inconsistent with the results for acetol). Results for the C-6 labeled case indicate that ~ 25% of the GA originates from C-5–C-6. The labeling results thus account for ~ 65% of all GA produced. The remaining fraction must originate from C-3–C-4 and/or from C-4–C-5.

The fact that the GA carbons show roughly equal enrichment in all of the cases considered suggests that label scattering via keto–enol tautomerism occurs in these mechanisms. After several days at room temperature in $D_2O$, GA showed no diminution of its $^1H$ NMR signals, indicating that deuterium exchange via keto–enol tautomerism occurs very slowly in the aqueous distillate solution (this stability of the GA signal was observed in both neutral solution and in the distillate fraction itself). Therefore, the observed label scattering must occur in the pyrolysis. Note that this does not limit consideration only to those mechanisms in which GA breaks away as the enol or as the enolate ion, since it could also break away as the aldehyde and rapidly tautomerize (via reversible enolization) while still in contact with the pyrolyzing sample. Alternatively, ionization of the hydroxyl group in the aldehyde form of GA would allow tautomerization via a 1,2-hydride shift[23]. Thus, most of the previously proposed mechanisms of GA formation discussed in the Introduction are still viable in light of the labeling results.

*GA from C-1–C-2.*—The reverse aldol reaction suggested by Shafizadeh and Lai[6] is one way to account for the 40% of GA arising from C-1–C-2. Their mechanism begins, however, with the assumption that LG serves as an intermediate in the formation of smaller compounds, and this assumption should probably be discarded, at least when considering vacuum pyrolysis, since the volatility of LG would cause it to vaporize quickly and leave the reaction zone as it is formed. Indeed, Houminer and Patai[19] demonstrated that LG simply distills under conditions of vacuum pyrolysis. Still worth considering, however, is the concept of reverse aldol reaction of the aldehyde form of glucose, which can arise by scission of a terminal glucosidic linkage (trace amounts of both anomers of glucose have been detected in the pyrolyzates of stereoregular glucans). The reverse aldol concept can be applied to a reducing end-group as well as to free monomer.

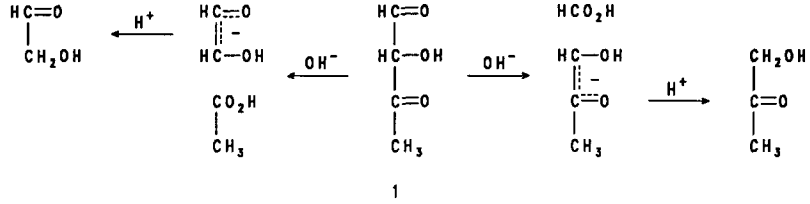
The formation of GA from C-1–C-2 by reverse aldol reaction of aldoses during alkaline degradation is well established[24] and quite conceivable as a pyrolytic reaction. Pyrolytic dehydration of the remaining four-carbon fragment, erythrose, to form the 2-hydroxy-3-oxobutanal (**1**) intermediate is also conceivable. Dehydration at C-5–C-6 can also occur when the original aldohexose unit is still in the pyranose ring form. That such exocyclic dehydrations probably occur in pyrolysis is made evident by the presence of pyrone derivatives such as 3-hydroxy-2-methyl-4-pyrone in cellulose pyrolyzates[9,25]. These concepts are illustrated in Scheme 1, which shows two possible pathways whereby glucose can yield GA from C-1–C-2 and **1** from C-3–C-4–C-5–C-6.



Scheme 1.

2-Hydroxy-3-oxobutanal (**1**) has been reported as a product from pyrolysis of various types of biomass[25–27], and significant yields of **1** were reported by Kaaden et al.[13] to be among the products from the pyrolysis of amylose treated with sodium hydroxide. The latter workers identified **1** by its mass spectrum in pyrolysis-GLC–MS experiments, preventing its decomposition on the column by operating at low temperatures (elution temperature for **1** was ~ 13°C). Shafizadeh and Lai[6] speculated that compound **1** decarbonylated to yield acetol, and this is consistent with the observation by Kaaden et al.[13] of a "positive correlation" between the molecular ion of acetol and that for **1** in the pyrolysis–field ionization mass spectra of carbohydrates[28], suggesting that **1** is an intermediate in the formation of acetol. However, pyrolytic decarbonylations of aliphatic aldehydes generally require[29] temperatures in excess of 500°C, and this process may not be important at the temperatures under consideration (250–350°C). An alternative and more attractive mode of degradation for compound **1** is hydrolysis, which would still yield acetol from C-4–C-5–C-6 (Scheme 2).

2-Hydroxy-3-oxobutanal (**1**) is a formylacylcarbinol which, like diacylcarbinols, is very susceptible to hydrolytic cleavage[30,31]. Scheme 2 illustrates the two possible modes of hydrolysis of **1**. The hydrolysis of formylacylcarbinol and diacylcarbinol intermediates has been invoked to explain the formation of many products in the alkaline degradation of carbohydrates, including formic acid from cellulose[15], 2-deoxytetronic acid from cellobiose[32], acetol from aldoses[33], and pyruvic acid



Scheme 2.

from glucose[34]. Scheme 2 shows that it is a nucleophilic substitution reaction in which hydroxide ion attacks one carbonyl group, and the adjoining fragment containing the other carbonyl group leaves as an enolate ion, which subsequently picks up a proton. In pyrolysis, the water can be provided by various concurrent dehydration reactions. As Scheme 2 shows, the attractive feature of compound **1** is that by hydrolysis it is capable of yielding all four of the major, small organic compounds produced by glucan pyrolysis. We have previously proposed that compound **1** can arise in a reaction pathway which competes with isosaccharinolactone formation[1], and it will be considered further in the course of this discussion.

Evidence that a major reaction pathway for GA is base-catalyzed is provided by the fact that when cellulose is pyrolyzed with 0.5% NaOH the GA yield is much higher than when it is pyrolyzed with 0.5% NaCl (Table V, pyrolysis conditions: 350°C for 30 min). These results suggest that the mechanisms whereby the four distillate compounds are formed are in general base-catalyzed, that they compete with LG formation, and that NaCl acts as a weak base (results of studies by Halpern and Patai[35] suggest that the latter effect could be due to loss of chloride ion during pyrolysis).

Another key feature of the formation of GA from C-1–C-2 by reverse aldol reaction is that it requires the aldehyde form of a reducing end-group. To test such a mechanism, cellobiose and cellobiitol (synthesized by $NaBH_4$ reduction of cellobiose[36]) were pyrolyzed in the presence of 1% NaOH for 30 min at 300°C and results are shown in Table VI. The table shows the pyrolytic yield of GA from

TABLE V

Vacuum pyrolysis of CF11 cellulose (% yield by weight) [a]

| | Untreated | 0.5% NaCl | 0.5% NaOH |
|---|---|---|---|
| Distillate | 9 | 32 | 47 |
| GA | < 0.1 | 4.9 | 10.4 |
| Acetol | Tr | 1.6 | 4.2 |
| HOAc | Tr | 0.4 | 1.2 |
| $HCO_2H$ | Tr | 0.6 | 1.5 |
| Tar | 84 | 15 | 10 |
| LG | 55 | 2 | 0.4 |

[a] Tr, trace.

TABLE VI

Vacuum pyrolysis of NaOH-treated disaccharides (% yield by weight) [a]

| | Cellobiose | Cellobiitol |
|---|---|---|
| Distillate | 46 | 33 |
| GA | 3.9 | 0.6 |
| Acetol | 0.9 | 0.6 |
| HOAc | 1.7 | 0.3 |
| $HCO_2H$ | 6.8 | nd |
| Tar | 29 | 33 |

[a] nd, not detected.

NaOH-pretreated cellobiose to be 6.5 times greater than its yield from similarly treated cellobiitol, a result which supports the importance of both reducing end-groups and base-catalysis.

To investigate whether a reducing end-group produces a greater proportion of GA from C-1–C-2 than does an in-chain group, a pyrolysis of labeled glucose was conducted. NaCl-treated 1-$^{13}$C-glucose (20% enriched) was vacuum pyrolyzed for 30 min at 300°C. The distillate fraction was analyzed by NMR, and the results show that ~60% of the GA produced arises from C-1–C-2. For NaCl-treated MeGpol, this figure is ~40% (Table IV). Thus, the importance of a reducing end-group in GA formation from C-1–C-2 is further substantiated.

Aside from the reverse aldol reaction, the only proposed mechanism that accounts for the 40% of GA from C-1–C-2 is that suggested by Byrne et al.[8], involving fragmentation of a glucopyranosyl cation end-group. The most speculative step in this mechanism is the initial C-2–C-3 bond scission. The closest precedent to this in the literature appears to be base-catalyzed fragmentation of 3-hydroxyalkyl halides and tosylates[37]. No attempt has been made to test this mechanism.

*GA from C-5–C-6.*—The labeling results show that ~25% of all GA produced arises from C-5–C-6. Consistent with this is the mechanism proposed by Shafizadeh and Lai[7], in which GA arises from C-5–C-6 via the thermal decomposition of 3-deoxy-D-*erythro*-hexosulose (**2**). 3-Deoxyaldosuloses are formed as general intermediate products in the acid- and alkali-catalyzed reactions of carbohydrates[38], and **2** has been shown to be an intermediate in the base-catalyzed formation of metasaccharinic acids from (1 → 3)-linked glucans[39]. Furthermore, this 3-deoxyhexosulose has been detected in the products of cellulose pyrolysis[22,40]. In the mechanism proposed by Shafizadeh, it undergoes reverse aldol reaction to form pyruvaldehyde and glyceraldehyde, the latter compound then undergoing disproportionation to yield GA form C-5–C-6. However, in a pyrolysis study of various glycoses by Heins and Klier[41], neither GA nor formaldehyde were detected in the products of the pyrolysis of glyceraldehyde. Moreover, the fact that up to 38% yield of metasaccharinolactone is formed during pyrolysis of a (1 → 3)-linked glucan[42] suggests that the primary pyrolytic fate of 3-deoxy-D-*erythro*-hexosulose

(2) is benzilic acid rearrangement rather than fragmentation. Therefore, the mechanism proposed by Shafizadeh and Lai[7] appears doubtful as a possible major pyrolytic pathway.

The mechanism suggested by Evans and Milne[9] is another proposal for obtaining GA from C-5–C-6. It begins with normal base-catalyzed ring-opening. However, instead of final protonation of the anionic center at O-5 to form an aldehyde glucose end-group, these authors proposed a C-4–C-5 bond scission, apparently driven by the electronegativity of the C-3 hydroxyl, which leaves as hydroxide. This is vaguely reminiscent of $\beta$-hydroxycarbonyl elimination, but in the latter case only pi electrons move along the carbon chain. The breaking of a sigma bond is quite another matter. There appears to be no precedent for such a step in the literature. Therefore, this appears to be an unlikely pyrolytic mechanism.

In the mechanism suggested by Richards[10], initial formation of a double bond between C-2 and C-3, which sets the stage for retro Diels–Alder reaction, can occur via either acid- or base-catalyzed dehydration and can involve the loss of either the 3-hydroxyl group or of the 2-hydroxyl group. The remaining four-carbon fragment, after the breaking away of GA, would still form part of the glucan chain. Having an enol ether group at each end, however, it might be expected to hydrolyze quickly and then tautomerize to 2-hydroxybutanedialdehyde (**3**). Compound **3** has been identified by its mass spectrum in cellulose pyrolyzate by Pouwels et al.[43]. These workers describe **3** as "possibly one of the key compounds in the thermal degradation of cellulose". Unfortunately they do not elaborate on this statement, and we have found no discussion of **3** in any of their previous or subsequent papers.

The proposal by Lomax et al.[11], is another electrocyclic mechanism whereby GA might arise from C-5–C-6. The authors describe this reaction as a "reverse aldolization fragmentation of a sugar residue", and from the point of view of the C-2–C-3 and C-4–C-5 bond scissions, it might be so regarded. However, the C-1–O-5 bond scission is certainly not a reverse aldol reaction, and a better way to describe the entire process would be a [2 + 2 + 2] cycloreversion. Woodward and Hoffmann[44] have demonstrated that thermally allowed pathways for such processes exist, and they cite literature precedents for them. Moreover, this process has been invoked to explain the formation of $m/z$ 204 ions in the mass spectral fragmentation of trimethylsilylated pyranose rings[45]. Detection of the permethylated derivatives of 4-*O*-ethanal glucopyranose, ethan-2-alyl glucopyranoside, and hydroxyethenyl glucopyranoside by Lomax et al.[11] in the permethylated products of Curie-point pyrolysis of cellulose offers strong support for such a mechanism. The presence of these compounds indicates that the C-1–C-2 and C-3–C-4 fragments frequently remain attached to the neighboring glucose rings as O-linked acetaldehyde units. Note that another possible fate of these two-carbon fragments, which exist initially as enol ethers, is hydrolysis to form additional molecules of GA. This would provide GA from C-1–C-2 and from C-3–C-4, which is quite consistent with the labeling results from the present study.

*Acetol.*—It was assumed in the analysis of the GLC–MS data that the carbonyl carbon of acetol could not originate from a terminal carbon (C-1 or C-6) by any mechanism, barring formation and recombination of free radicals. In support of this assumption, no isotopic enrichment of the carbonyl carbon was apparent in the distillate spectra from 1-$^{13}$C-MeGpol and 6-$^{13}$C-MeGpol, whereas such enrichment could be clearly seen in the distillate spectrum from 1-$^{13}$C-MeGpol. In general, the labeling results show that pyrolytically produced acetol derives most often from contiguous terminal carbons (C-1–C-2–C-3 or C-4–C-5–C-6), and the acetol methyl groups most often derive from a terminal carbon (C-1 or C-6). These are the same general results obtained by Hayami and co-workers[46] in their labeling study of the origins of acetol from degradation of hexoses in aqueous solution, and this similarity of results suggests a similarity of mechanistic processes. To explain their results, Hayami et al.[33] invoked a mechanism involving formation and hydrolysis of a six-carbon diacylcarbinol intermediate analogous to **1**.

The labeling experiments apparently account for all of the acetol produced in the pyrolysis of NaCl-treated MeGpol. Fig. 2 illustrates the main sources of acetol and approximate amounts from each source, the principal orientation being shown in each case. It follows from these results that acetol is produced by at least three different major reaction pathways, i.e., that acetol arises from three different segments of the glucose ring. For each of these segments, both orientations for the derived acetol occur, but one always predominates, especially in the case of the C-4–C-5–C-6 segment, over 90% of the acetol from that segment possessing methyl groups from C-6. The formation of acetol from the 2-hydroxy-3-oxobutanal (**1**) in Scheme 1 is consistent with this result. In the 20% of acetol which derives from C-2–C-3–C-4, C-2 is the origin of most of the hydroxymethyl carbons. Consistent with this result is the formation of acetol by the type of fragmentation

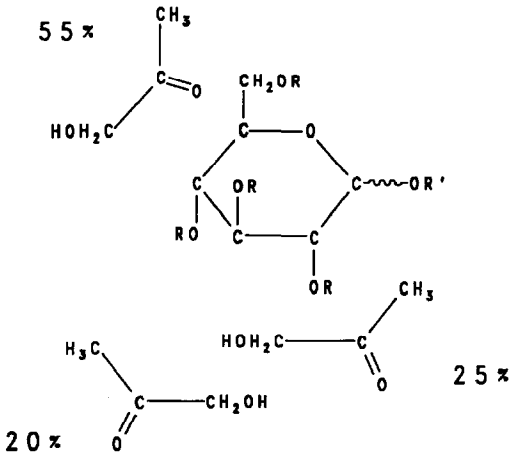
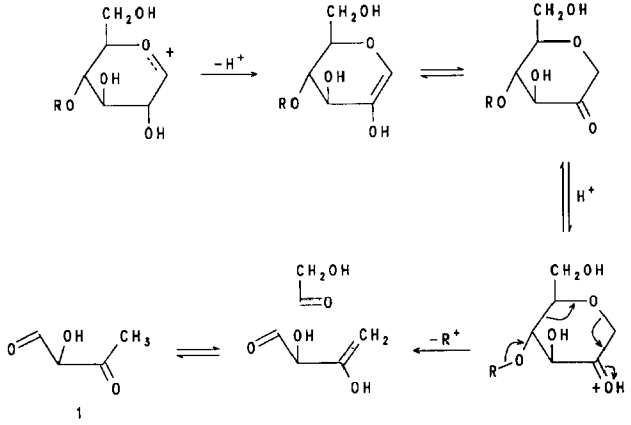



Fig. 2. Pyrolytic sources of acetol from MeGpol.

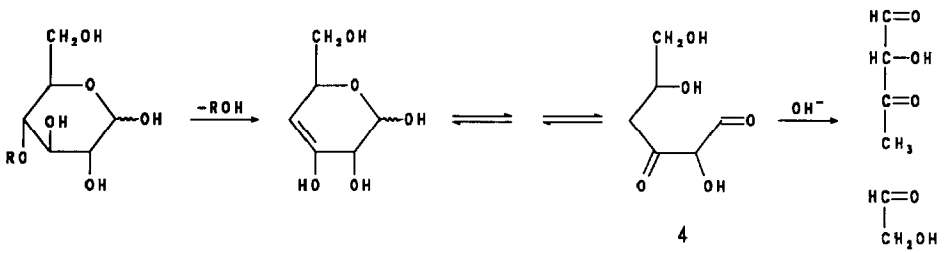


Scheme 3.

previously proposed for the 4-deoxy-3-hexosulose intermediate which will be present in equilibrium with the 4-deoxy-2,3-hexodiulose intermediate leading to isosaccharinolactone[1]. Roughly 25% of the acetol comes from C-1–C-2–C-3, and in this context, Scheme 3 illustrates another way of deriving 2-hydroxy-3-oxobutanal (**1**) from thermal degradation of a glucan, in this case by ring fragmentation of a 2-oxo end-group which can arise by deprotonation of a glucosyl cation end-group. By this process the methyl group in the acetol produced by hydrolysis of **1** would come from C-1, as required by the labeling results.

*Acetic acid.*—Table IV shows that ~30% of the acetic acid derives from C-1–C-2. By comparison, the C-2 labeling results indicate that ~25% of the acetic acid arises from C-2–C-3 and/or from C-1–C-2. Thus, the C-2–C-3 segment is of minor importance as a source of acetic acid. This situation is reminiscent of the analogous labeling results for GA, and seems to support the view of Kang et al.[12] that acetic acid is produced from GA via ketene. However, it is known that the label is about evenly distributed in GA, and that this distribution occurs during pyrolysis. Therefore, if GA is a precursor for acetic acid then, barring the possibility of an isotope effect of unlikely magnitude in the dehydration–rehydration process, the label would have to be about evenly distributed between the two carbons in acetic acid, and this is not the case. Table IV also shows that ~45% of the acetic acid derives from C-5–C-6. (The labeling work thus accounts for ~80% of all acetic acid produced from pyrolysis of NaCl-treated MeGpol.) Therefore, C-5–C-6 is the most important source of acetic acid, whereas C-1–C-2 is the most important source of GA, a difference which is incompatible with the idea that one compound arises from the other. The evidence thus indicates that the major pathways to acetic acid are independent of GA formation.

The concept of a common pathway leading to both acetic acid and acetol is attractive. These are the two compounds possessing methyl groups, and in both cases, the principal sources are segments of a glucose unit which include a terminal



Scheme 4.

carbon (C-1 or C-6), that terminal carbon generally ending up as the methyl carbon in the product. This correlation suggests a common intermediate in major pathways leading to these two compounds, and such an intermediate might be 2-hydroxy-3-oxobutanal (**1**). The methyl group of **1** arising in Schemes 1 and 3 is derived from C-6 and C-1, respectively, so that the acetic acid or acetol arising from **1** via hydrolysis in either scheme conforms with the labeling results.

*Formic acid.*—Table IV shows that nearly half of the formic acid produced from pyrolysis of NaCl-treated MeGpol derives from C-1. Moreover, C-2 and C-6 are shown to be minor sources of formic acid. Therefore, the remainder (nearly half) must come from C-3, C-4, and/or C-5. In a previous paper[1], the possibility of isomerization of the isosaccharinic acid precursor to form a 4-deoxy-3-hexosulose (**4**) intermediate was considered. As shown in that paper, **4** is a very attractive intermediate from the point of view of the four small compounds under consideration, since it degrades by simple and well established mechanisms to yield all of them. The low pyrolytic yields of isosaccharinolactone from (1 → 4)-linked glucans[1] suggests a low pyrolytic rate of formation of its 4-deoxy-2,3-hexodiulose precursor. However, pyrolytic formation of **4** can conceivably occur by pathways other than that leading to isosaccharinolactone. For instance, elimination of ROH (R = glucan chain) from a (1 → 4)-linked glucopyranosyl end-group followed by ring opening would directly yield **4** as shown in Scheme 4. That such elimination occurs in pyrolysis is made evident by the presence of such products as 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-enitol-3-ulose in glucan pyrolysates[47]. Scheme 4 also shows how **1** and GA can result from reverse aldol reaction of **4**.

*Trihydroxybenzenes.*—In addition to providing information on the pyrolytic formation of one-, two-, and three-carbon compounds, the present labeling work has shed some light on the formation of phenols from glucans. Trihydroxybenzenes (THB) are among the volatile components of glucan pyrolysis[1]. Two isomers, 1,2,4-THB and 1,2,3-THB, are found in the tar fraction. Their yields are enhanced by addition of NaCl, and the 1,2,4-isomer always predominates. This apparently is true for all glucans and for aldohexosans generally. In the case of cellulose, the THB isomers are accompanied by smaller amounts of the 1,2- and 1,4-isomers of dihydroxybenzene (DHB)[48]. The mechanism of THB formation is unknown. It has been previously suggested that they might arise by recombination of free radicals[48],

although it is also possible that direct hexose to aromatic ring conversion occurs. Previous work with a variety of glucans[1] has shown that THB formation is generally insensitive to the types of glucosidic linkages present in the glucan, and previous work with cellulose[48] has shown that it is generally insensitive to temperature as well.

The pyrolysis of isotopically labeled glucans offered an opportunity to further investigate the question of THB formation. Mass spectra of the $Me_3Si$-derivatized THB isomers formed during pyrolysis of 1-$^{13}$C-MeGpol, 2-$^{13}$C-MeGpol, and 6-$^{13}$C-MeGpol were analyzed, and the results showed that the THB isomers from labeled glucans are labeled to the same extent as the glucans themselves, although the degree of enrichment of individual carbons could not be determined due to the simplicity of the mass spectra. This suggests that the THB isomers arise from six-carbon fragments which derive intact from the glucose rings. The direct hexose to aromatic ring concept is thus strongly supported.

An obvious prerequisite for conversion of an aldohexose to a carbocycle is initial opening of the pyranose ring. One possible mechanism whereby the resulting hexose chain can then close to form a six-carbon ring is intramolecular aldol condensation. Dehydration at C-5–C-6, either before or after ring opening, can lead to the required 1,5-dicarbonyl precursor (cf. Scheme 1) [for (1 → 6)-linked glucans, this would involve elimination of ROH]. Aldol condensation of that precursor results in a polyhydroxy–cyclohexanone intermediate. Most of the likely dehydration pathways leading from the intermediate to phenols result in 1,2,4-THB, and the rest result in 1,2,3-THB (none of them result in 1,3,5-THB), thus accounting for the distribution of THB isomers. This scheme has close analogies with synthetic work by Ferrier[49] in which a hex-5-enopyranoside derivative was made to undergo carbocyclic ring closure to form a cyclohexanone derivative, which was subsequently converted to a 1,2,4-THB derivative. A weakness of the scheme is that it fails to account for the formation of dihydroxybenzenes. The 1,2- and 1,4-isomers of DHB are apparently formed by a mechanism that involves a reduction step.

## SUMMARY AND CONCLUSIONS

It has long been recognized that many of the same compounds formed during pyrolysis of cellulose and of other glucans are also formed during degradation of these same glucans in aqueous solution. For example, the anhydro sugars and furan derivatives formed in acidic aqueous solutions are also formed pyrolytically, highest yields being obtained when potentially basic impurities have been removed. Likewise, dehydration and fragmentation products characteristic of aqueous alkaline degradation are also found in the pyrolyzates of base-catalyzed pyrolyses. The results of this work have shown that the major one-, two-, and three-carbon compounds can derive from a variety of sources in glucan pyrolysis. Considering only the major sources, these results expand the parallels between pyrolysis and

TABLE VII

Possible sources of **1** and of its hydrolysis products

| Scheme number | Original glucose carbon numbers in **1** CHO–CHOH–CO–$CH_3$ | | | | Hydrolysis products of **1** |
|---|---|---|---|---|---|
| 4 | 1 | 2 | 3 | 4 | GA from C-1–C-2 and HOAc from C-3–C-4<br>Or acetol from C-2–C-3–C-4 and $HCO_2H$ from C-1 |
| 3 | 4 | 3 | 2 | 1 | GA from C-3–C-4 and HOAc from C-1–C-2<br>Or acetol from C-1–C-2–C-3 and $HCO_2H$ from C-4 |
| 1 | 3 | 4 | 5 | 6 | GA from C-3–C-4 and HOAc from C-5–C-6<br>Or acetol from C-4–C-5–C-6 and $HCO_2H$ from C-3 |

solution chemistry of polysaccharides. Thus, formic acid from pyrolysis is derived mainly from C-1, in accordance with proposed alkaline degradation mechanisms. Also acetol (hydroxypropanone) derives from the hexose units of glucans by pyrolytic pathways that resemble those of alkaline degradation of hexoses. A principal source of glycolaldehyde is shown to be C-1–C-2, in accordance with known reverse aldol reactions in solution. Acetic acid is shown to form independently of GA formation, and, as in the case of acetol, the principal pyrolytic sources of acetic acid from glucans are shown to be consistent with mechanisms involving hydrolytic cleavages of diacylcarbinol intermediates like those which have been proposed as intermediates in aqueous alkaline degradation. In fact, the labeling results for all major one-, two-, and three-carbon products can be shown to conform generally to simple mechanisms involving hydrolytic cleavage of a formylacylcarbinol intermediate (**1**) previously identified in the products of base-catalyzed pyrolyses. Table VII summarizes the three schemes proposed for pyrolytic formation of **1**. For each scheme, the table lists the carbon numbers in **1** corresponding to the original glucose ring, and the origins of the possible hydrolysis products of **1**. All of the latter are consistent with the labeling results.

Extrapolation of the results of the labeling work with the synthetic glucan to pyrolysis of stereoregular glucans such as cellulose is only valid to the extent that linkage types are largely irrelevant. This effect is least valid for six-carbon pyrolysis products. Thus, for example, the dependence of metasaccharinolactone yield upon the presence of (1 → 3)-linkages in the original glucan is a striking example of linkage-dependence[42]. However there is an apparent linkage-independence in the formation of one-, two-, and three-carbon compounds, though admittedly, this could be due to the multitude of possible pathways leading to each compound, and in fact the relative importance of the different pathways could be linkage-dependent. Thus, the fact that the labeling study found many different sources for each compound could be a result of the presence of many different types of glycosidic linkages in the synthetic glucan. Analysis of the pyrolysis products of a labeled stereoregular glucan might reveal fewer major sources for these compounds. Limited work has been conducted in this area. For example, pyrolytic studies of

milligram quantities of 1- and 2-$^{13}$C-labeled bacterial cellulose, using molecular beam mass spectrometry, have been conducted by Evans and co-workers[50], and results indicate that C-1 is not an important source of glycolaldehyde. Further such studies are clearly needed for gaining a better understanding of cellulose pyrolysis[51].

## EXPERIMENTAL

*Materials and general methods.*—$^{13}$C-labeled glucose was purchased from Isotec Inc., glucose from J.T. Baker Chemical Company, and cellobiose from Pfanstiehl Laboratories. The latter was deionized using a mixed-bed resin, this procedure resulting in the removal of 90% of the indigenous metal ions (measured by inductively coupled argon plasma spectrometry). $^{13}$C NMR and $^{1}$H NMR spectra were recorded at room temperature at 22.5 and 90 MHz, respectively, using $D_2O$ as solvent. GLC separations were performed with a Hewlett–Packard 5890A gas chromatograph using He as the carrier gas. The column was a Hewlett–Packard Ultra-1 capillary column (0.20 mm i.d., 25 m, 0.33 $\mu$m crosslinked methyl silicone) operating isothermally at 70°C. Mass spectra were obtained with a Hewlett–Packard 5970 mass selective detector interfaced with a Hewlett–Packard 9133 computer. Vacuum pyrolyses were performed as described previously[52].

*NMR analysis.*—The use of 16K data points for $^{13}$C NMR spectra enabled reproducible relative peak area measurements ($\pm$5%) using a 1750 Hz window from 18 to 95 ppm. This window includes signals for four carbons of interest: the aldehyde (hydrate) and hydroxymethyl carbons of GA and the methyl and hydroxymethyl carbons of acetol. $^{13}$C quantification of each of these carbons in labeled distillate spectra was achieved by calibrating their completely decoupled $^{13}$C signals relative to $Me_2SO$ internal standard using solutions of known concentrations. GA standard solutions were designed to model actual concentrations in the NMR solutions of the distillates, thus avoiding different equilibria with other forms at higher concentrations[53]. Completely decoupled $^{13}$C NMR spectra of the standards were obtained, the signals were integrated, and the area ratios (area of particular carbon/area of $Me_2SO$ signal) were plotted against the corresponding known mmol ratios to obtain calibrations for each of the four carbons. The $R^2$ values for the calibration plots are greater than 0.99. $^{13}$C NMR spectra of the pyrolysis distillates were obtained using the same parameters as those used for the calibration standards. Multiplication of the area ratio for each carbon by the slope of the respective calibration plot gives the apparent mmol ratio, which when multiplied by the mmol of $Me_2SO$ in that distillate, gives the apparent mmol of that carbon present. The latter figure is then multiplied by 11 to give the $\mu$mol of $^{13}$C (natural abundance of $^{13}$C = 1.1%). The $\mu$mol of $^{12}$C for each carbon is determined from the proton spectrum (by integration relative to $Me_2SO$), since protons on $^{13}$C give rise to satellite signals[54] and thus do not contribute to the area of the main signal which is due solely to protons on $^{12}$C. Although protons on a $^{12}$C atom may be coupled to adjacent $^{13}$C atoms, such geminal ($^{13}$C–C–H) or

vicinal ($^{13}$C–C–C–H) coupling is likely to be 5 Hz or less. Although a selected resonance may be broadened by such coupling, its integrated intensity will not be altered. Using the $\mu$mol of $^{13}$C and the $\mu$mol of $^{12}$C, the amount of $^{13}$C arising from the label can be calculated. The degree of enrichment, expressed as a decimal fraction, is given by $E = X/T$, where $X$ is the $^{13}$C arising from the label, and $T$ is the total $\mu$mol ($^{13}$C and $^{12}$C). Since the original glucan is 20% enriched at a specific carbon, the degree to which any carbon in the pyrolyzate arises from that labeled position is given by 5 $E$, or in terms of percentage 500 $E$. Application of this method to the pyrolysis distillate of an unlabeled glucan is expected to show no enrichment for each carbon, and thus provides a test of the method.

To determine enrichment for the acids, the distillate fractions from two or four pyrolyses of the labeled glucan were combined and neutralized to pH 7.5 with 0.025 M NaOH, and the resulting solution was evaporated to dryness. The residue was then dissolved in $D_2O$ containing sodium maleate and $Me_2SO$ as internal standards. Enrichment values for the formate carbon and the acetate methyl carbon were then determined as described above. The formate carbon was calibrated relative to maleate, and the acetate carbon was calibrated relative to $Me_2SO$. To calibrate the formate and acetate carbons, a series of standard solutions of known concentrations containing both sodium salts and the internal standards were prepared. Completely decoupled $^{13}$C NMR spectra of these standard solutions using a 4000 Hz window from 17 to 195 ppm provided data for the calibration plots for which $R^2$ values are greater than 0.99.

Table VIII lists completely decoupled $^{13}$C chemical shifts of the distillate components, of the sodium salts of the acids, and of internal standards used in this study. All shifts were measured relative to $Me_2SO$ at 40 ppm. Only pertinent signals are listed in some cases.

*GLC–MS analysis.*—Distillate fractions destined for GLC–MS analysis were rinsed out of the cold trap with an aliquot (0.3 mL) of deionized water. This solution (0.2 $\mu$L) was injected directly onto the GLC column. Formic acid, GA, acetic acid, and acetol eluted at ~2.7, 2.9, 3.1, and 3.3 min, respectively. In the

TABLE VIII

NMR chemical shifts in $D_2O$ (ppm)

| | $^1$H NMR | $^{13}$C NMR |
|---|---|---|
| GA [a] | 3.48 (d, 5.0), 5.00 (t) | 65.8, 91.0 |
| Acetol | 2.11 (s), 4.31 (s) | 26.1, 68.8, 213.3 |
| HOAc | 2.04 (s) | 21.6, 177.7 |
| $HCO_2H$ | 8.18 (s) | 166.8 |
| Na acetate | 1.85 (s) | 24.3 |
| Na formate | 8.38 (s) | 172.0 |
| Na maleate | 5.95 (s) | 131.4 |
| DMSO | 2.68 (s) | 40.0 |

[a] Hydrated monomer.

TABLE IX

MS data for compounds analyzed for isotopic enrichment

| | |
|---|---|
| $HCO_2H$ | 28 (27), 29 (100), 44 (11), 45 (37), 46 (43) |
| HOAc | 31 (6), 41 (6), 42 (22), 43 (100), 45 (94), 60 (38) |
| Acetol | 31 (24), 43 (100), 74 (6) |
| $Me_3Si$-1,2,3-THB | 73 (100), 239 (80), 342 (50) |
| $Me_3Si$-1,2,4-THB | 73 (95), 239 (58), 342 (100) |

total ion chromatogram, the GA and acetic acid peaks overlapped, and the GA peak was of very low intensity, apparently due to the fact that most of the GA was polymerizing on the column. Because of the low intensities of the relevant ions, and because of interference by the same ions in acetic acid, the GA mass spectrum was unsuited for enrichment determinations.

The degree of enrichment of a mass spectral ion, expressed as a decimal fraction, is given by $E = (A - B)/(A + AB - B)$, where $A$ is the M/M + 1 ratio for unlabeled case, and $B$ is that ratio for the labeled case. Since the original glucan is 20% enriched at a specific carbon, the degree to which an ion arises from a source that includes that labeled carbon is given by 5 $E$, or in terms of percentage 500 $E$. Enrichment of the methyl carbon of acetic acid was arrived at by simply taking the difference between the enrichment of the molecular ion and that for the carboxyl ion. Enrichment of the methyl carbon of acetol was regarded as equal to that for the acetyl ion in the cases of C-1 label and C-6 label, since the carbonyl carbon of acetol could not derive from a terminal carbon of glucose. In the case of C-2 label, the enrichment of the acetyl ion of acetol derives from two sources: enrichment of the methyl carbon in acetol molecules that come from C-2–C-3–C-4, and enrichment of the carbonyl carbon in acetol molecules that come form C-1–C-2–C-3. Since an estimate of the latter quantity is known from analysis of the C-1 labeled case, the enrichment of the methyl carbon of acetol in the C-2 labeled case can be calculated. Signal intensities were read from tabulations printed by the computer. Where necessary (e.g., because of contamination by $O_2$ or because of extraneous overlapping peaks), background corrections were made. Mass spectral data for the isotopically enriched compounds analyzed by mass spectrometry in this study are shown in Table IX. Major $m/z$ values are listed with signal intensities in parentheses.

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