

## Thermal Degradation of 6-Chloro Carbohydrates

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### Synopsis

It has been shown that 6-chloro sugar derivatives are thermally less stable than the corresponding unsubstituted carbohydrates. When heated, they generate hydrogen chloride which catalyzes a series of heterolytic reactions including transglycosylation, dehydration, inter- and intramolecular etherification, and condensation. The latter products are ultimately carbonized through free-radical reactions producing large amounts of char.

### INTRODUCTION

It has been shown that heating of reducing sugars results in thermal anomerization<sup>1-5</sup> and polymerization.<sup>1,2,4</sup> The same type of polymeric materials is formed through the thermal transglycosylation of anhydrosugars,<sup>6,7</sup> glycosides,<sup>2,8-11</sup> oligosaccharides,<sup>4</sup> and polysaccharides.<sup>6,11</sup> On further heating, the intermediate products are decomposed through a series of dehydration, fission, disproportionation, condensation, and charring reactions.<sup>1,10-13</sup> The concurrent and consecutive pyrolytic reactions could be catalyzed through the addition of acidic or alkali reagents.<sup>2,10-14</sup>

For flameproofing of cellulosic materials,<sup>15</sup> various types of acidic and halogenated compounds are used to promote the acid-catalyzed dehydration and charring reactions and reduce the production of volatile organic products which fuel rapidly spreading flaming combustion.<sup>16</sup>

In view of the academic and technological aspects of this subject, 6-chloro-6-deoxy- $\alpha$ -D-glucopyranose and the related methyl and phenyl  $\alpha$ - and  $\beta$ -D-glycosides have been investigated as model compounds to determine the effect of chlorine as a leaving group and a potential source of hydrogen chloride during the pyrolytic reactions.

### EXPERIMENTAL

#### Analytical Procedure

To unravel the sequence of the thermal reactions, dynamic methods of thermal analysis are used to detect the temperature range of different thermal events. The nature of the physical or chemical transformations are subsequently determined by other parallel isothermal or scanning analytical methods.

Melting point determination, thermal analysis, UV (ultraviolet), IR (in-

frared), ESR (electron spin resonance), mass spectroscopy, GLC (gas-liquid chromatography) and TLC (thin-layer chromatography) were conducted by the methods and equipment described in previous publications.<sup>2,8,13</sup> Dynamic thermal analysis experiments were programmed at the rate of 15°C/min. The glycosidic compounds in the reactions mixture and the tar fraction of the pyrolysis products were hydrolyzed by boiling 1M hydrochloric acid for 8 hr, and the monomeric products were analyzed by GLC as usual.<sup>4</sup>

### Preparation of Model Compounds

Methyl 6-chloro-6-deoxy- $\alpha$ - and - $\beta$ -D-glucopyranosides were prepared by deacetylation of the corresponding acetate derivatives through a modification of the previously described method.<sup>17</sup> The  $\alpha$ -D anomer was recrystallized from ethyl acetate and had mp 113–114°C (lit.<sup>18</sup> 113–114°C). The  $\beta$ -D anomer after crystallization from absolute ethanol had mp 156–157°C (lit.<sup>19</sup> 156–157°C). Phenyl 6-chloro-6-deoxy- $\beta$ -D-glucoside was prepared similarly and recrystallized from water, mp 169–170°C; found: C, 51.76%, H, 5.49%; calcd for C<sub>12</sub>H<sub>15</sub>O<sub>5</sub> Cl: C, 52.45%, H, 5.46%. 6-Chloro-6-deoxy- $\alpha$ -D-glucopyranose was also prepared as described before<sup>17</sup> and crystallized from ethanol-ethyl acetate-diethyl ether (1:5:5), mp 132–135°C (lit.<sup>20</sup> 135–136°C). Samples of methyl  $\alpha$ - and  $\beta$ -D-glucopyranosides were obtained from a commercial source.

Methyl 3,6-anhydro- $\alpha$ - and - $\beta$ -D-glucopyranosides, the corresponding furanosides, and 3,6-anhydro-D-glucose used in the following experiments as reference compounds were synthesized by the published method.<sup>21</sup>

Samples of the 6-chloro sugar and glycosides containing 50% sodium carbonate were obtained by grinding the calculated proportions of the two compounds to a fine powder in a mortar. Samples containing 5% zinc chloride were prepared by adding the calculated proportion of catalyst in methanol and evaporating the solvent under vacuum.

### Thermal Reactions

Samples (~2 mg) of the model compounds with and without the catalysts were heated in a DTA (differential thermal analysis) cell at the rate of 15°C/min to elevated temperatures corresponding to various thermal events. The heated samples were then trimethylsilylated and analyzed by GLC using inositol as the internal standard and the known compounds for reference. The results obtained are listed in Tables I and II.

### Pyrolysis Products.

The volatile products formed on programmed heating of 6-chloro- $\alpha$ -D-glucopyranose, methyl 6-chloro-6-deoxy- $\alpha$ - and - $\beta$ -D-glucopyranosides, and phenyl 6-chloro-6-deoxy- $\beta$ -D-glucopyranoside were swept with a gentle stream of nitrogen through a solution of alcoholic silver nitrate to recover the hydrogen chloride as silver chloride and a saturated solution of DNPH (2,4-dinitrophenylhydrazine) in 2N HCl to recover the carbonyl compounds as the DNPH derivatives. Precipitation of silver chloride began at the initial de-

composition temperature of each sample (Figs. 1a, 1c, and 2; Table IV). The precipitate of mixed DNPH derivatives was filtered, washed with 1N HCl and water, and analyzed by TLC<sup>22</sup> using silica gel (IB-F Baker-flex) plate. The individual carbonyl products were identified by comparison with known

TABLE I  
Analysis of Mixtures Formed on Heating of 6-Chloro-6-Deoxy- $\alpha$ -D-Glucopyranose to Different Temperatures

Temperature °C	Remaining 6-chloro-6-deoxy-D-glucopyranose forms (%)			$\frac{\alpha \times 100}{\alpha + \beta}$
	$\alpha$ -	$\beta$ -	$\alpha + \beta$	
20.0	99.2	0.8	100.0	99.2
123.5	95.7	2.6	98.3	97.4
133.0	80.5	17.5	98.0	82.1
137.5	28.5	22.8	51.3	55.6
142.0	12.8	8.8	21.6	59.1
146.0	6.6	7.4	14.0	47.1
150.0 <sup>a</sup>	0.0	0.0		

<sup>a</sup> Used for acid hydrolysis of the resulting condensation products.

TABLE II  
Pyrolysis Products of 6-Chloro-6-deoxy- $\alpha$ -D-glucopyranose (I),  $\alpha$ - and  $\beta$ -Forms of Methyl 6-Chloro-6-deoxy-D-glucopyranoside (II and III), and Phenyl 6-Chloro-6-deoxy- $\beta$ -D-glucopyranoside (IV) at 500°C

Product	Yield (%)			
	I	II	III	IV
Methanol	T <sup>a</sup>	16.2	17.8	T
Acetic acid	0.7	1.5	0.9	0.4
$\alpha$ -Angelica lactone	T	0.1	T	T
2-Furaldehyde	0.2	0.2	0.2	0.1
2,3-Benzofuran	—	—	—	0.3
5-Methyl-2-furaldehyde	0.7	1.7	1.2	0.6
2-Furfuryl alcohol	T	T	T	T
$\beta$ -Angelica lactone	0.6	0.8	0.7	0.4
Phenol	—	—	—	28.0
Levulinic acid	2.5	2.2	2.3	2.0
Total acid (HCl, carboxylic acid)	22.0	18.0	18.2	—
Carbon dioxide	5.0	3.1	2.5	3.0
Water	12.0	9.0	9.0	5.0
Char	31.8	28.3	34.0	27.8
Tar	15.4	20.6	15.0	9.6
Before acid hydrolysis				
I and its $\beta$ -form	T			
II		T	T	
III		T	T	
IV and its $\beta$ -form				T
After acid hydrolysis				
I and its $\beta$ -form	(22.5) <sup>b</sup>	(25.2)	(15.0)	(4.6)
D-glucose	(4.3)	(T)	(T)	(T)
3,6-anhydro-D-glucose	(2.3)	(10.5)	(5.5)	(7.0)
3,6-anhydro-D-glucose isomer	(9.0)	(20.0)	(30.0)	(21.0)

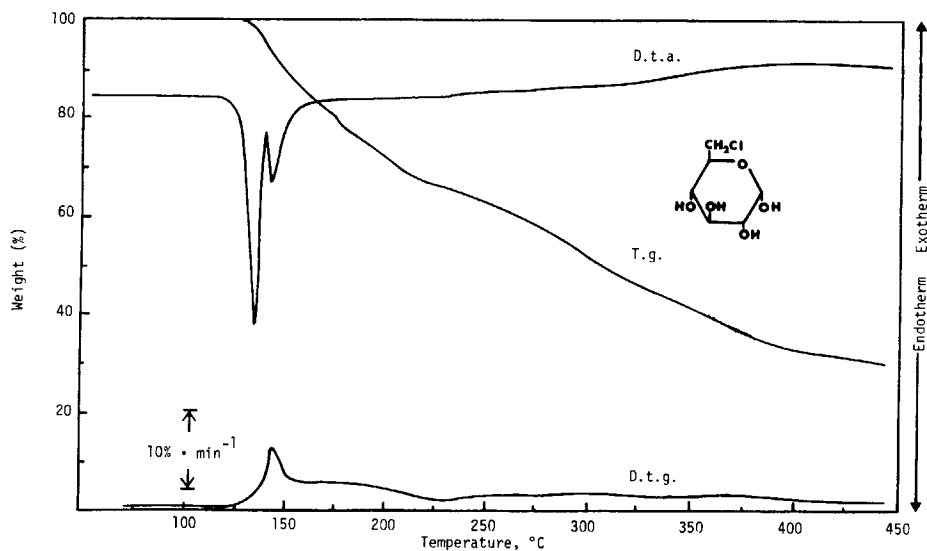
<sup>a</sup> Trace amounts.

<sup>b</sup> Numbers in parentheses are percentages of the tar fraction.

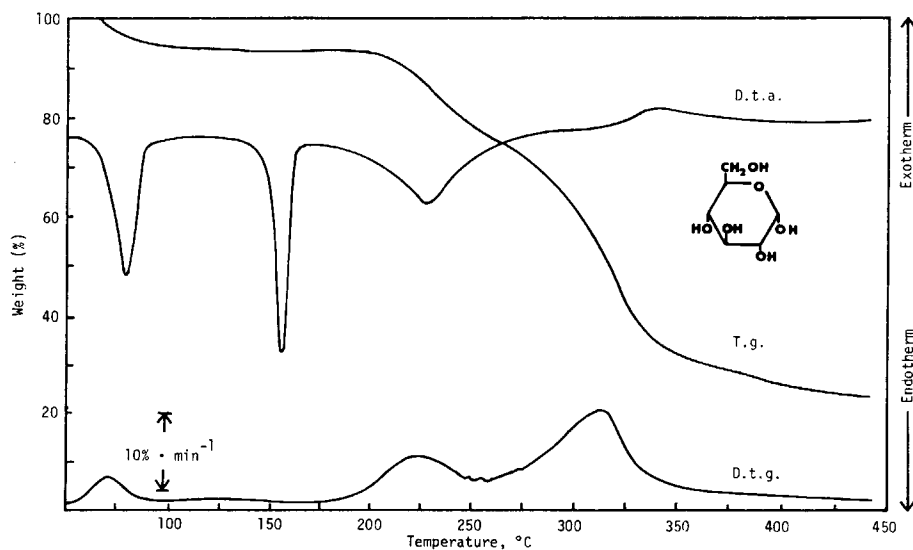
compounds and color development with ethanolamine.<sup>22</sup> All the chlorinated compounds gave DNPH derivatives of 5-(hydroxymethyl)-2-furaldehyde, 2-furyl hydroxymethyl ketone, 2-furyl methyl ketone, 5-methyl-2-furaldehyde, and 2-furaldehyde.

### Scanning Mass Spectrometry

Methanol, methyl chloride, water, carbon dioxide, and other low molecular weight, volatile products evolved on gradual heating of the model compounds

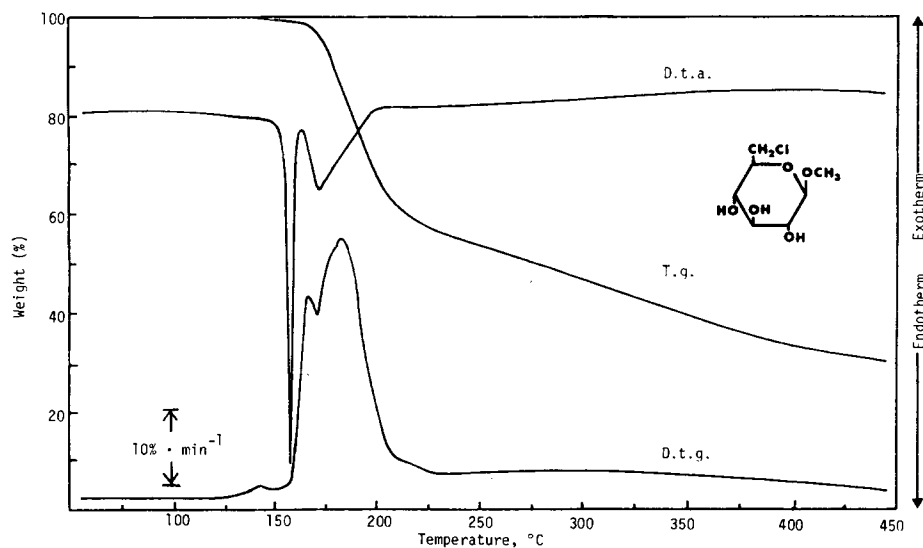


(a)

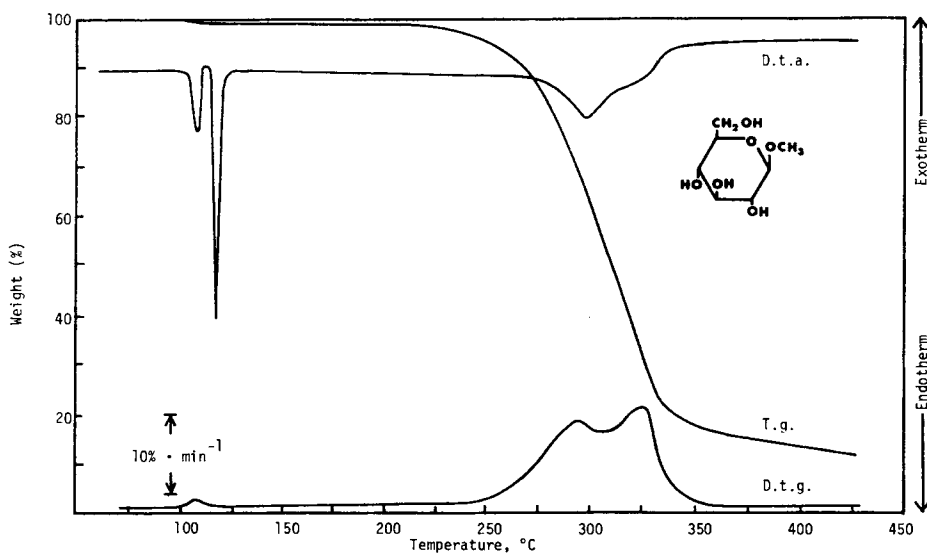


(b)

Fig. 1 (continued)



(c)



(d)

Fig. 1. Thermal analysis curves of some D-glucose derivatives: (a)  $\alpha$ -D-glucopyranose, (b) 6-chloro-6-deoxy- $\alpha$ -D-glucopyranose, (c) methyl 6-chloro-6-deoxy- $\beta$ -D-glucopyranoside, and (d) methyl  $\beta$ -D-glucopyranoside.

were monitored by concurrent mass spectrometry as described previously.<sup>13</sup> The results obtained for methyl 6-chloro-6-deoxy- $\beta$ -D-glucopyranoside are illustrated in Figure 2. A similar pattern was obtained for the corresponding  $\alpha$ -D-anomer, except that the peaks occurred at a higher temperature near 220°C.

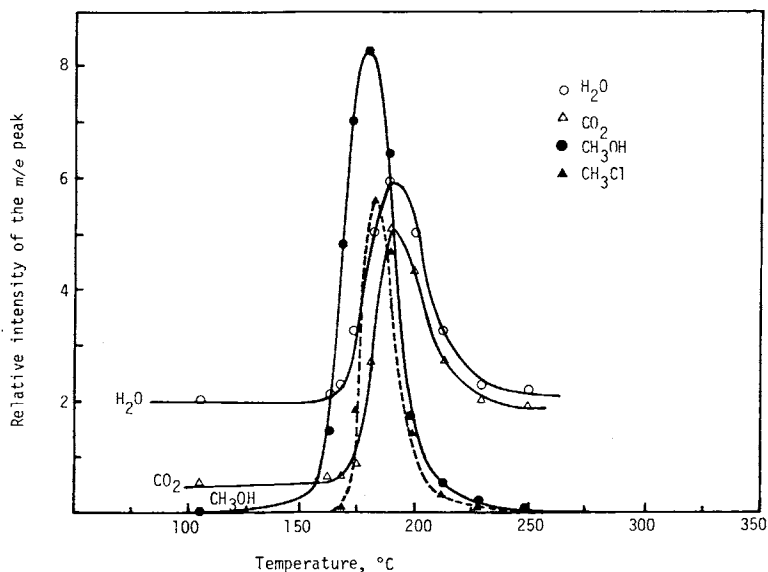


Fig. 2. Evolution of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$  on heating of methyl 6-chloro-6-deoxy- $\beta$ -D-glucopyranoside.

### Isothermal Pyrolysis

Samples ( $\sim 100$  mg) of each of the model compounds were heated under nitrogen for 8 min at  $500^\circ\text{C}$  in a modified Sargent microcombustion unit, and the products were separated and analyzed by the methods described in a previous publication.<sup>12</sup> The total amounts of acid, calculated as hydrogen chloride, were obtained by titrating the volatiles with  $0.1N$  solution of sodium hydroxide. For direct analysis of the volatile and water, small samples (5 mg) of the chlorinated compounds were pyrolyzed at  $500^\circ\text{C}$  in a pyrolysis unit directly connected to a gas chromatograph. The products were resolved in GLC and identified by established methods.<sup>7,11,23</sup> The results are given in Table III.

## RESULTS

### 6-Chloro-6-deoxy- $\alpha$ -D-glucopyranose

Thermal analysis of this compound (Fig. 1a) shows a major endotherm centered at  $133^\circ\text{C}$  corresponding to the melting point of the sugar. This peak is partially overlapped with a smaller endotherm at  $140^\circ\text{C}$  that is accompanied by 17% weight loss and a sharp DTG (derivative thermogravimetry) peak at  $142^\circ\text{C}$ . Further heating gives a steady rate of weight loss, characteristic for gradual charring,<sup>13</sup> and leaves 35% of a carbonaceous residue at  $400^\circ\text{C}$ .

The broad melting endotherm indicates a simultaneous transformation of the 6-chloro sugar, similar to the thermal anomerization observed for other reducing sugars.<sup>2,4</sup> The course of this transformation was investigated by trimethylsilylation and GLC of samples heated to different temperatures corresponding to various stages in the development of the overlapping endotherm.

TABLE III  
Analysis of Mixtures Formed on Heating of the  $\alpha$ - and  $\beta$ -Forms of  
Methyl-6-chloro-6-deoxy-D-glucopyranoside to Different Temperatures

Temperature °C	Methyl 6-chloro-6-deoxy-D-glucopyranoside, %		Methyl 3,6-anhydro- $\alpha$ -D-glucoside, %		Methyl 3,6-anhydro- $\beta$ -D-glucoside, %	
	$\alpha$ -	$\beta$ -	Pyrano-	Furano-	Pyrano-	Furano-
$\alpha$ -Form						
Neat	220	93.0	—			
	225	15.3	T <sup>a</sup>			
	230	0.0	0.0			
+ZnCl <sub>2</sub>	120	95.8	—			
	130	75.7	T			
	140	62.7	4.4			
	150	6.8	2.1			
+Na <sub>2</sub> CO <sub>3</sub>	180	83.5		2.5		
	190	47.5		33.5		
	210	5.9		51.8	T	
	240	0.8		45.5	T	
$\beta$ -Form						
Neat	165	T	82.5			
	170	6.3	41.7			
	180	3.4	17.6			
	190	2.7	12.6			
	200 <sup>b</sup>	T	5.1			
+ZnCl <sub>2</sub>	137	T	84.4			
	142	5.7	57.0			
	145	13.4	20.1			
	147	14.7	8.4			
	152	6.9	2.1			
+NaCO <sub>3</sub>	225		60.5		20.8	
	240		11.6		51.4	T
	250		2.4		43.5	T
	260		T		32.4	3.0

<sup>a</sup> Trace amounts.

<sup>b</sup> Used for acid hydrolysis of the resulting condensation products.

erms. The resulting data, presented in Table I, showed transformation of the  $\alpha$ -D to the  $\beta$ -D-form as well as a gradual conversion of both forms to other materials. TLC of the reaction mixtures containing these materials showed a continuous strip between the starting point and the location of the 6-chloro sugar, indicating conversion of the reducing sugar to nonvolatile, heterogeneous condensation products. A sample, heated to 150°C, corresponding to the conclusion of the decomposition endotherm, did not contain any monomeric compound, but on acid hydrolysis produced about 40% monosaccharides, consisting mainly of 6-chloro-6-deoxy-D-glucose (18.5%), isomers of 3,6-anhydro-D-glucose<sup>10,13</sup> (14%), and D-glucose (6.8%). This experiment showed that the condensation reactions involve glycosyl polymerization and inter- and intramolecular displacement of the chlorine by hydroxyl groups, producing 3,6-anhydro-D-glucose and D-glucose moieties. Intermolecular condensations involving nonglycosidic groups account for the low yield of the monomeric products. Also, the nonglycosidic condensation products account for

the large amount of charred residue, because on further heating, they are not broken down by intramolecular transglycosylation and remain to be charred and carbonized through the cleavage of the substituents and the free-radical reactions, which take place at higher temperatures.<sup>8,10,12,15</sup>

Evolution of the volatile products at different temperatures was studied by sweeping the nitrogen purge gas through a solution of alcoholic silver nitrate to recover the hydrogen chloride as silver chloride, or through a solution of acidic DNPH to recover the carbonyl compounds as the DNPH derivatives. Formation of silver chloride started at about 137°C corresponding to the initial decomposition of the molecule. TLC analysis of the DNPH derivatives showed the presence of a variety of dehydration products, including 5-(hydroxymethyl)-2-furaldehyde, 2-furyl hydroxymethyl ketone, 2-furyl methyl ketone, 5-methyl-2-furaldehyde, and 2-furaldehyde.

Isothermal pyrolysis at 500°C provided a cross section of the products formed by the sequence of pyrolytic reactions. These products, listed in Table II, consisted of a tar fraction containing a trace amount of the original compound and larger quantities of its condensation products, hydrochloric acid, water, carbonaceous char, carbon dioxide resulting from disproportionation of the molecule,<sup>12,23</sup> and a variety of volatile organic compounds. GLC analysis of the volatiles showed a significant proportion of levulinic acid, smaller quantities of 4-hydroxy-3-pentenoic, and 4-hydroxy-2-pentenoic acid  $\gamma$ -lactones ( $\alpha$ - and  $\beta$ -angelica lactones, respectively), and furan derivatives derived from dehydration reactions.<sup>24</sup>

The total amount of acids produced (21.5%) was slightly higher than a theoretical yield of hydrogen chloride (18.37%) because it includes some organic acids.

The preponderant formation of water, levulinic acid, and furan derivatives, and ultimately char, shows the effect of chlorine as a leaving substituent in the molecule and the simultaneous production of hydrogen chloride in catalyzing the dehydration, condensation, and carbonization reactions. The same type of catalytic effect has been shown for zinc chloride as a Lewis acid additive.<sup>10</sup> This effect is readily visible when the thermal analysis curves of the 6-chloro compound (Fig. 1a) are compared with those of the parent sugar, which is thermally more stable (see Fig. 1b). The normal sugar,  $\alpha$ -D-glucopyranose, is polymerized at 225°C, and the polymer is decomposed rather sharply at  $\sim$ 300°C leaving less char. Furthermore, the polymerization products consist almost entirely of D-glucose units.<sup>5</sup>

### Methyl 6-chloro-6-deoxy- $\beta$ -D-glucopyranoside

In the absence of the reducing group, thermal analysis curves of methyl 6-chloro-6-deoxy- $\beta$ -D-glucopyranoside (Fig. 1c) show a sharp melting endotherm at 156°C, which is followed by a broad decomposition endotherm centered at 170°C and accompanied by 40% weight loss. A steady rate of weight loss on continued heating leaves 34% of carbonaceous residue at 400°C. Comparison with the corresponding normal glycosides (see Figs. 1c and 1d) shows that the 6-chloro derivative is thermally less stable. It decomposes at some 130°C lower and gives more char (34% instead of 14%).

The initial decomposition reactions and weight loss within the range of



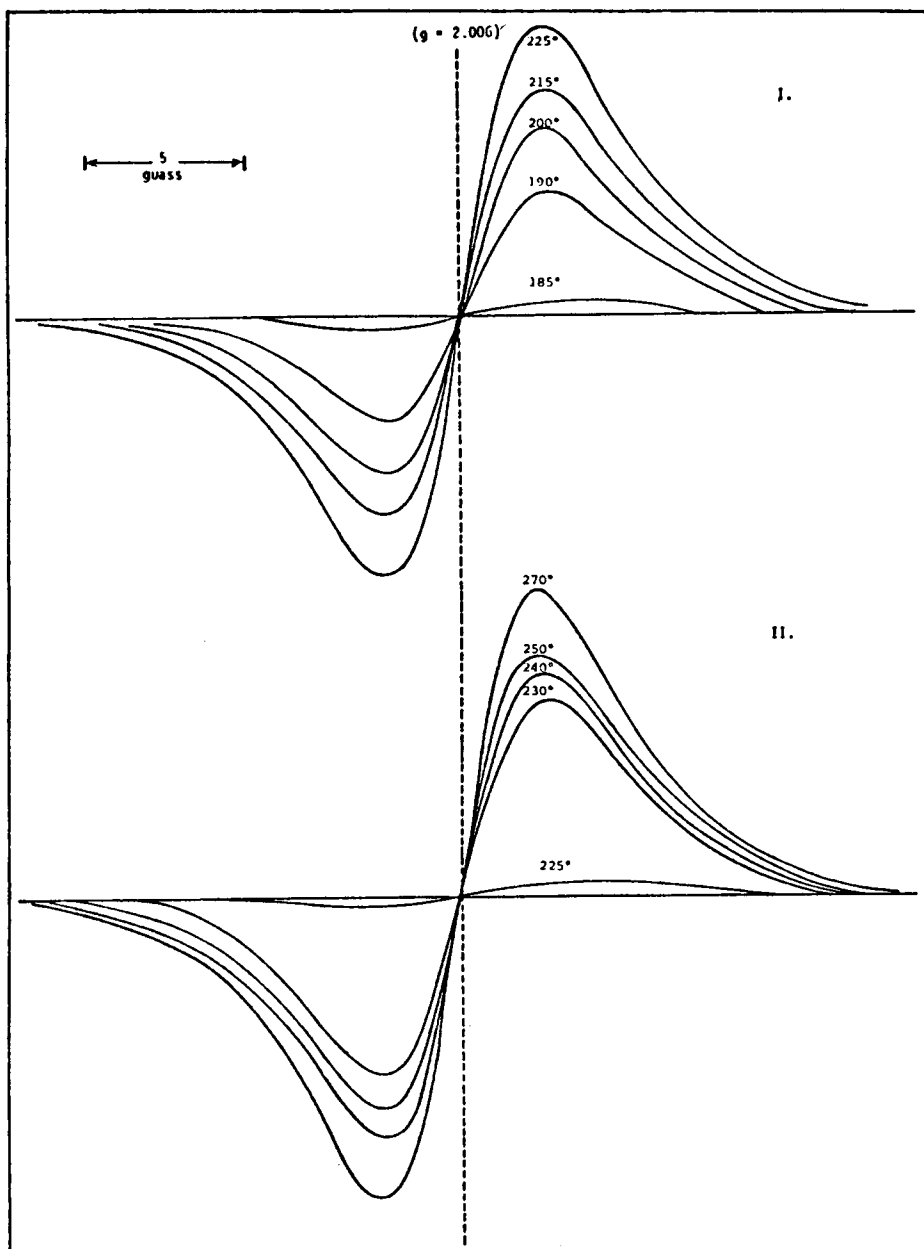


Fig. 3. ESR signals formed on heating of methyl 6-chloro-6-deoxy- $\beta$ -D-glucopyranoside (I) and the  $\alpha$ -D anomer (II) to various temperatures at the rate of  $\sim 15^\circ\text{C}/\text{min}$ .

150–225°C were investigated by monitoring the volatile products and analyzing the residues. Scanning mass spectrometry of the gases formed at different temperatures (see Fig. 2) showed the evolution of methanol ( $m/e$  31), methyl chloride ( $m/e$  50), water ( $m/e$  17), and carbon dioxide ( $m/e$  44), reaching the maximum rate at  $\sim 180^\circ\text{C}$ , corresponding to the development of the decomposition endotherm. Production of methyl chloride is not mechanisti-

TABLE IV  
Thermal Analysis Features of Chlorinated and the  
Corresponding Unsubstituted Glycosides

Additive <sup>a</sup>	DTA peaks		DTG peaks	TG
	Mp, °C	Dec., °C	Dec., °C	Residue at 400°C, %
Methyl 6-Chloro-6-deoxy- $\alpha$ -D-glucopyranoside				
Neat	114	220, 225 <sup>b</sup>	220	32
+ZnCl <sub>2</sub>	—	150, 165	155	40
+Na <sub>2</sub> CO <sub>3</sub>	112	210, 250 <sup>b</sup>	200	20
Methyl 6-Chloro-6-deoxy- $\beta$ -D-glucopyranoside				
Neat	156	170	170 <sup>c</sup> , 185	34
+ZnCl <sub>2</sub>	—	150	150 <sup>c</sup> , 158	38
+Na <sub>2</sub> CO <sub>3</sub>	151	250, 268 <sup>b,c</sup>	200 <sup>c</sup> , 250	20
Methyl $\alpha$ -D-Glucopyranoside				
Neat	167	290, 320	295, 320	17
+ZnCl <sub>2</sub>	165	~205, ~235, 257 <sup>b</sup>	185, 220	41
+Na <sub>2</sub> CO <sub>3</sub>	162	285 <sup>b</sup> , 310 <sup>b</sup>	277	22
Methyl $\beta$ -D-Glucopyranoside				
Neat	115	305, 330	295, 325	14
+ZnCl <sub>2</sub>	105	~175, 220, 237 <sup>b</sup>	175, 220	41
+Na <sub>2</sub> CO <sub>3</sub>	100, 115 <sup>c</sup>	280 <sup>b</sup> , 300 <sup>b</sup>	90, 270	12
Phenyl 6-Chloro-6-deoxy- $\beta$ -D-glucopyranoside				
	167	178	182	32
Phenyl $\beta$ -D-Glucopyranoside <sup>8,10,14</sup>				
Neat	176	305, 330	311, 336	12
+ZnCl <sub>2</sub>	140	140, ~200, 220 <sup>b</sup>	160, ~200, 220	49
+NaOH		230, 270, <sup>b</sup> 320 <sup>b</sup>	230, 290	24

<sup>a</sup> 5% ZnCl<sub>2</sub> and NaOH, and 50% Na<sub>2</sub>CO<sub>3</sub>.

<sup>b</sup> Exothermic.

<sup>c</sup> A shoulder.

cally significant because it may be formed from a secondary interaction of methanol and hydrogen chloride, both of which have been found among the pyrolysis products (see Table II).

The GLC analysis of the residue (see Table III) showed a gradual decomposition of the  $\beta$ -glycoside accompanied with production of some  $\alpha$ -form due to catalyzed anomerization.<sup>2,10</sup> A sample heated to 200°C contained only a trace of unreacted glycoside, was partially soluble in water, and showed TLC streaks characteristic of heterogeneous condensation products.<sup>2,13</sup> This sample also showed UV absorption with maxima at 220 and 290 nm, and an IR absorption band at 1720 cm<sup>-1</sup> for carbonyl groups. On acid hydrolysis, it gave 6 chloro-D-glucose (19.5%), 3,6-anhydro-D-glucose (6.2%) and its isomer (11%),<sup>10,13</sup> with a trace of D-glucose, showing that condensation of the 6-chloro glycoside involves inter- and intramolecular displacement of the chlorine atom in addition to the thermal transglycosylation observed for normal glycosides.<sup>2,8-11</sup> Decomposition and carbonization of the condensation products on further heating was investigated by ESR spectrometry. ESR scanning of

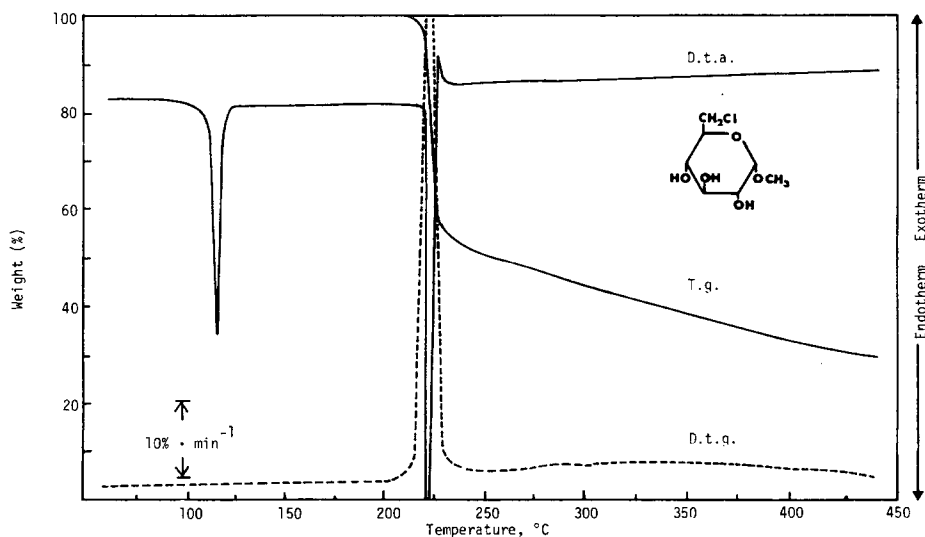


Fig. 4. Thermal analysis curves of methyl 6-chloro-6-deoxy- $\alpha$ -D-glucopyranoside.

the pyrolysis residues within the range of 50–235°C indicated that initial decomposition reactions are heterolytic, but charring reactions which take place above 190°C are accompanied with the formation of stable free radicals (Fig. 3).

Chemical analysis of the volatile products during the initial decomposition showed the production of hydrogen chloride recovered as silver chloride, and the same carbonyl compounds obtained as DNPH derivatives from 6-chloro-6-deoxy- $\alpha$ -D-glucose. Isothermal pyrolysis of the methyl 6-chloro glucoside at 500°C also gave the same type of results that were obtained for the 6-chloro-D-glucose under similar conditions (Table II).

#### Effects of Acidic and Alkaline Additives

Addition of zinc chloride to methyl 6-chloro-6-deoxy- $\beta$ -D-glucopyranoside enhanced the anomerization (Table III), lowered the decomposition temperature to 150°C, and produced more char (38% at 400°C) (Table IV).

Addition of an excessive amount of sodium carbonate (1:1 by weight) neutralized the autocatalytic effect of the liberated hydrogen chloride. As shown in Tables III and IV, it shifted the decomposition peak from 170° to 250°C and produced substantial amounts of methyl 3,6-anhydro- $\beta$ -D-glucopyranoside. The facile formation of the 3,6-anhydro compound indicated that the intramolecular displacement of the halogen, which is well known for aqueous systems,<sup>21</sup> also prevails under pyrolytic conditions.

#### Other 6-Chloro Glucosides

Closely similar data, including thermal analysis (Table IV), DNPH derivatives, and pyrolysis products (Table II), were obtained for phenyl 6-chloro-6-deoxy- $\beta$ -D-glucopyranoside. However, the phenyl glucoside showed a sharper decomposition endotherm and produced a small amount of benzofuran

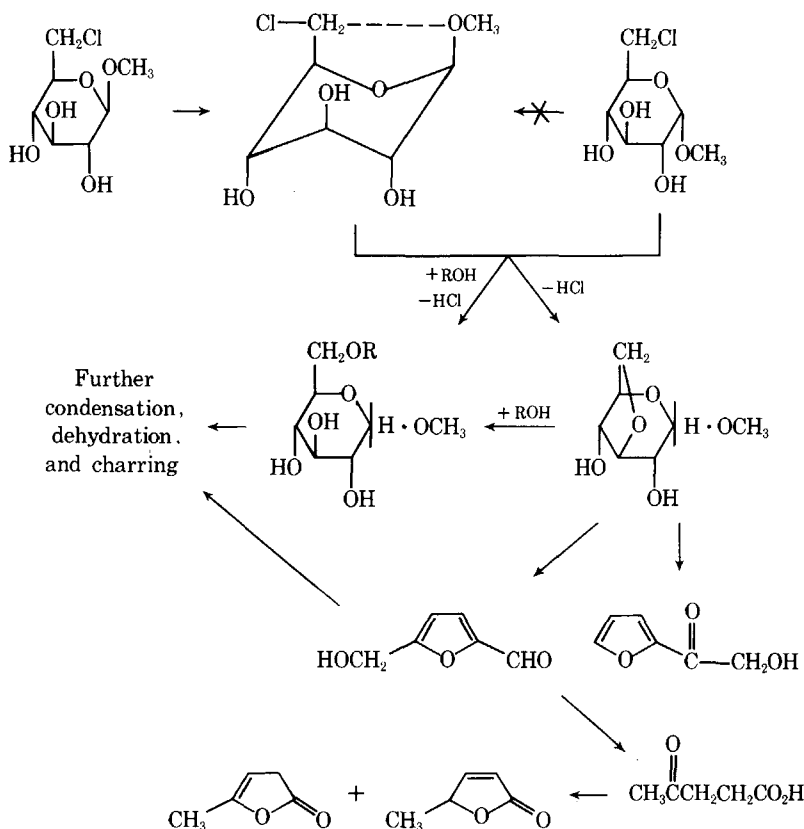
(Table II). As observed for acid catalyzed pyrolysis of phenyl  $\beta$ -D-glucopyranoside,<sup>10,25</sup> this compound is formed from simultaneous fission and dehydration of the sugar moiety without cleavage of the glycosidic link.

Methyl 6-chloro-6-deoxy- $\alpha$ -D-glucopyranoside also gave the same dynamic and isothermal pyrolysis data that were obtained for methyl 6-chloro-6-deoxy- $\beta$ -D-glucopyranoside (Tables II, III, and IV and Fig. 1c), with the notable exception that the  $\alpha$ -D anomer was more stable and decomposed very sharply at 200°C instead of 170°C (Fig. 4). However, the difference in stability disappeared on addition of zinc chloride and was even reversed on addition of sodium carbonate (Table IV).

Scanning mass spectrometry of volatiles showed the evolution of the same compounds as noted for the  $\beta$ -D anomer (Fig. 2), but the peak for hydrogen chloride ( $m/e$  36) was distinctly developed, and the maximum rates occurred at the higher decomposition temperature ( $\sim 200^\circ\text{C}$ ).

### CONCLUSIONS

The above data show that heating of 6-chloro sugar derivatives results in dehydrohalogenation and rapid decomposition of the molecule at considerably lower temperatures than the decomposition range of the corresponding unsubstituted compounds shown in Table IV.



Scheme I. Thermal reactions of methyl 6-chloro-6-deoxy- $\alpha$ - and  $\beta$ -D-glucopyranoside

The unusually fast initial reaction (see Figs. 1a, 1c, and 4) involves intra- and intermolecular displacement of the combined halogen by hydroxyl groups and formation of ether-linked condensation products which are subsequently charred.

The released hydrogen chloride exerts a further autocatalytic effect in promoting the dehydration, condensation, and charring reactions, which have been shown to be acid catalyzed.<sup>10,13</sup>

When the hydrogen chloride is neutralized, the displacement reaction takes place at a higher temperature and provides large amounts of methyl 3,6-anhydro-D-glucopyranoside as an intermediate product. The pyrolytic reaction of the 3,6-anhydro compounds,<sup>26,27</sup> which is known to produce 5-(hydroxymethyl)-2-furaldehyde and 2-furyl hydroxymethyl ketone, and the higher reactivity of the  $\beta$ -D anomer provide further clues to the sequence of the pyrolytic reactions which are summarized in Scheme I. In this scheme, the higher reactivity of the  $\beta$ -D anomer is attributed to the formation of a five-membered cyclic glucosyloxonium ion,<sup>28-30</sup> which provides anchimeric assistance to the displacement of chlorine. The distinct configurational effect of the  $\beta$ -D anomer disappears under acid or alkali conditions, which support alternative mechanisms for displacement of the glycosidic group and the halogen.

The implication of these reactions on thermal decomposition of cellulose will be discussed in a following communication.

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