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THERMAL DECOMPOSITION OF METHYL α-D-GLYCOPYRANOSIDES

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ABSTRACT

Thermal analysis, coupled with chemical studies, indicates that methyl α-D-glycopyranosides undergo thermal decomposition in two overlapping stages. At lower temperatures, the major reaction is loss of the methoxyl group as methanol, and intra- or inter-molecular condensation of the glycosyl portion of the molecule. At higher temperatures, the predominant reaction is fragmentation of the transglycosylation products. Both reactions were found to be dependent on the configuration of the starting methyl α-D-glycopyranoside.

INTRODUCTION

Thermal decomposition of most carbohydrates occurs between 250–400°, and the major reactions that occur are transglycosylation and fragmentation[1–3]. Much of what we know about the mechanism of the transglycosylation reaction has come from studies of glycosides. Shafizadeh and co-workers[4–6] have shown that the thermal stability of phenyl glycosides decreases in the following order: phenyl β-D-glucopyranoside > phenyl β-D-xylopyranoside > phenyl 2-deoxy-α-D-*arabino*-hexopyranoside > phenyl 2-amino-2-deoxy-β-D-glucopyranoside > phenyl 2-acetamido-2-deoxy-β-D-glucopyranoside. The major, volatile product, formed in almost quantitative yield, was phenol, which indicates that one of the major reactions is cleavage of the glycosidic bond. It was also found that electron density at the glycosidic oxygen atom was important. Rate studies, using various para-substituted-phenyl β-D-glucopyranosides, indicated that the rates increase as the electron-withdrawing ability of the para substituent increases[5]. Both of these results are consistent with a heterolytic mechanism involving cleavage of the bond between the glycosyl and aglycon groups.

In the present study, the purpose was to determine the effect of the configuration of the glycosyl moiety upon the rate and products of the thermal-decomposition reaction. This information, plus the results of earlier studies, should lead to a better insight into the mechanism of the thermal decomposition of carbohydrates. The compounds used in this study were a series of methyl α-D-glycopyranosides. Rates and products of decomposition were determined by thermal-analysis techniques, in parallel with chemical studies.

RESULTS

The thermogram of methyl α-D-glucopyranoside is shown in Fig. 1, where the t.g. (thermogravimetry) and d.t.g. (derivative thermogravimetry) curves indicate the weight-loss and rate of weight-loss as the carbohydrate was heated at a constant rate of 10°/min. For methyl α-D-glucopyranoside, weight loss begins at 250° and proceeds very rapidly, leaving a residue of 13% at 500°. The d.t.g. curve indicates two peaks, a small peak centered at 294°, which corresponds to ~25% weight-loss, and a larger peak centered at 327°, which corresponds to the remaining weight-loss.

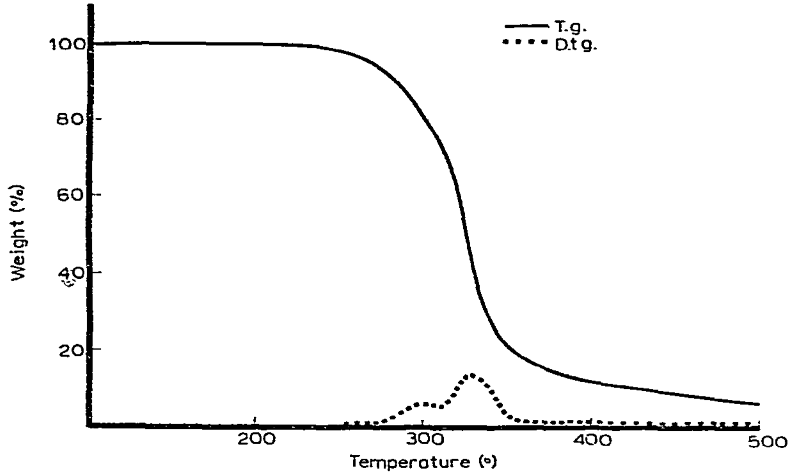

Fig. 1. Thermogram of methyl α-D-glucopyranoside.

TABLE I

THERMAL-ANALYSIS FEATURES OF METHYL α-D-GLYCOPYRANOSIDES

Compound	Melting point (degrees)		D.t.g. peaks		T.g.a. data	
	Reported	Found	1st peak (degrees)	2nd peak (degrees)	5% Weight-loss (degrees)	Residue at 500°
Methyl α-D-glucopyranoside	165–166	163–165	294	327	263	13
Methyl α-D-galactopyranoside	111	110–111	276	321	253	19
Methyl α-D-mannopyranoside	190–192	189–191	259	312	249	17
Methyl α-D-gulopyranoside	77	79–80	234	309	239	15
Methyl α-D-altropyranoside	107–108	105–107	237	321	237	7

The thermal data for methyl α-D-galactopyranoside, and the α-D-*manno*, α-D-*gulo*, and α-D-*altro* isomers are summarized in Table I; the thermograms had the same general shape. However, the initial temperature (5% weight-loss) and the temperature of the first and second d.t.g. maxima varied with the structure of the glycoside. The first maximum for the glucopyranoside occurred at 294°, the galactopyranoside at 276°, the mannopyranoside at 259°, the gulopyranoside at 234°, and the altropyranoside at 237°. The relationship between the temperature of the second d.t.g. maximum and the configuration was similar, except for methyl α-D-altropyranoside.

The thermal data described above were obtained by measuring weight-loss at a constantly increasing temperature. Isothermal decomposition was then studied at 227° (Fig. 2) between 0–20% weight-loss, which corresponds to the first d.t.g. peak. Trends similar to those observed by dynamic thermal analysis were observed. The glucopyranoside decomposes at the slowest rate, followed by the galactopyranoside, mannopyranoside, gulopyranoside, and finally the altropyranoside.

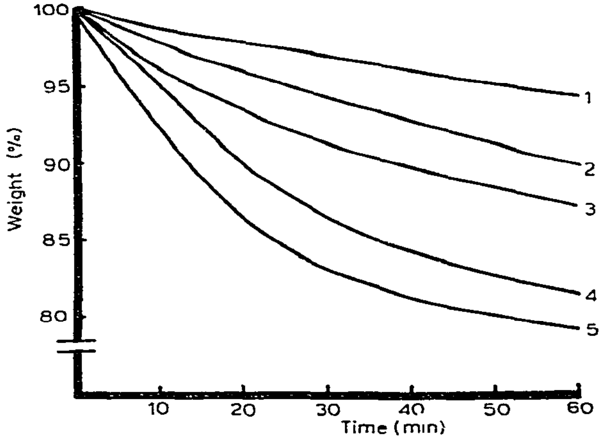

Fig. 2. The relative rates of isothermal weight-loss at 227° of a series of methyl α-D-glycopyranosides: 1, methyl α-D-glucopyranoside; 2, methyl α-D-galactopyranoside; 3, methyl α-D-mannopyranoside; 4, methyl α-D-gulopyranoside; 5, methyl α-D-altropyranoside.

In order to determine the changes occurring during the thermal decomposition, samples of methyl α-D-glucopyranoside were heated to different extents of weight-loss, and the amount of residual starting-material was then determined directly by silylation and g.l.c. analysis. The results (Fig. 3) indicate that the starting glycoside decomposed very rapidly and was completely gone after 27% weight-loss, which corresponds to the first peak of the d.t.g. curve. The major, volatile compound formed during this reaction was methanol.

The nature of the remaining non-volatile material was established by g.l.c. studies. After 20% weight-loss, the only monosaccharide present in the residue was a small amount of starting material and a trace of 1,6-anhydro-β-D-glucopyranose. However, large amounts of glucose were released by hydrolysis, indicating that the degraded material was a polymer (glucan) built up from glucose residues.

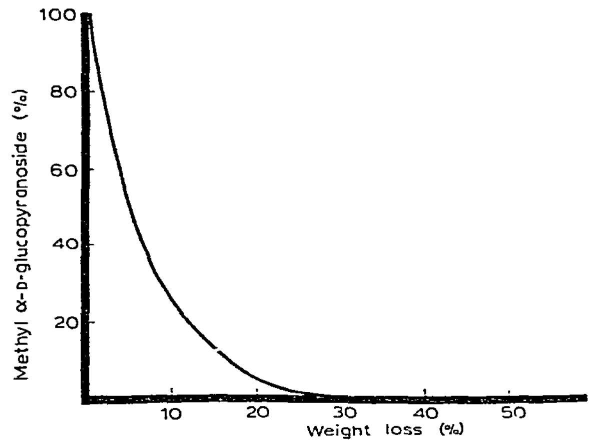

Fig. 3. The relationship between the concentration of the starting material (methyl α-D-glucopyranoside) and weight-loss.

This analysis was repeated with the other glycosides after heating in the t.g.a. instrument until ~20% weight-loss. The amounts of starting material and 1,6-anhydro sugar were determined directly by silylation and g.l.c. analysis, while the total amount of carbohydrate material was determined by the same procedure after hydrolysis with acid. The results of this analysis are summarized in Table II. Under these conditions, each glycoside was completely decomposed, with the exception of methyl α-D-glucopyranoside. For the methyl α-D-gluco-, -galacto-, and -manno-pyranosides, the only non-volatile product was a glycan, but for methyl α-D-gulo- and -altro-pyranosides, a mixture of glycan and 1,6-anhydro sugar was formed. Apparently, very little fragmentation had occurred within the pyranose ring, since >90% of the glycosyl units originally present in the glycosides could be recovered as the free sugar after hydrolysis of the polymer.

TABLE II

COMPOSITION OF THE MIXTURE OBTAINED BY HEATING METHYL α-D-GLYCOPYRANOSIDES

Compound	*Weight-loss (%)*	*Starting material (%)*	*Anhydro sugar (%)*	*Total carbohydrate (by hydrolysis) (%)*
Methyl α-D-glucopyranoside	22.8	2.8	0.0	92
Methyl α-D-galactopyranoside	17.5	0.0	0.0	93
Methyl α-D-mannopyranoside	19.7	0.0	0.0	95
Methyl α-D-gulopyranoside	21.5	0.0	9.0	~90
Methyl α-D-altropyranoside	17.9	0.0	46.0	—

The sequence of events occurring during thermal decomposition is initiated by cleavage between the methoxyl and glycosyl group, followed by liberation of the methoxyl group as methanol and condensation of the glycosyl group with another sugar molecule, or with HO-6 to form a 1,6-anhydro sugar. The second step of the reaction involves fragmentation of the glycan, or anhydro sugar, into a variety of compounds of low molecular weight.

DISCUSSION

The order and magnitude of the configurational effects indicate that the rate of decomposition parallels the overall conformational instability of the molecule. These results are similar to those found for acid hydrolysis[7,8]. The rates of acid hydrolysis and thermal decomposition are compared in Table III. For both reactions, the rates increase as the conformational instability increases; however, the rates of thermal decomposition are affected more for those glycosides containing an axial HO-2 group (methyl α-D-manno- and -altro-pyranoside). The conformation also affects the products in a similar manner. When methyl glycopyranosides are hydrolyzed with acid, the rate-determining step involves formation of a carbonium ion. The ultimate fate of this ion depends on the configuration of the molecule. Methyl α-D-gluco-, -galacto- and -manno-pyranosides form the corresponding free sugar, whereas methyl α-D-gulo- and -altro-pyranosides give a mixture of free sugars and the 1,6-anhydro-β-D-hexopyranose[9,10]. During thermal decomposition, the methyl α-D-gluco-, -galacto-, and -manno-pyranosides give a glycan, whereas methyl α-D-gulo- and -altro-pyranosides give mixtures of the glycan and 1,6-anhydro-β-D-hexopyranose.

TABLE III

THE EFFECT OF THE GLYCOSYL GROUP ON THE RELATIVE RATES OF ACID HYDROLYSIS[14] AND ON THERMAL DECOMPOSITION

Compound	*Relative rate of acid[a] hydrolysis*	*Relative rate of thermal[b] decomposition*
Methyl α-D-glucopyranoside	1.0	1.0
Methyl α-D-galactopyranoside	5.3	1.8
Methyl α-D-mannopyranoside	2.4	3.1
Methyl α-D-gulopyranoside	58.1	4.5
Methyl α-D-altropyranoside	18.0	6.2

[a]With 0.5M hydrochloric acid at 75°. [b]At 227°

The resulting rate data are also consistent with a direct displacement reaction of the aglycon by HO-6. This mechanism, which would lead to a 1,6-anhydro sugar, was originally proposed by Parks[11] to explain the thermal decomposition of cellulose. Even though no 1,6-anhydro sugars were isolated from the decomposition of methyl glycosides of glucose, galactose, and mannose, this does not mean that they were not formed. These three anhydro sugars would probably be less stable, due to their greater conformational instability, and more likely to polymerize than the 1,6-anhydro sugars formed from methyl α-D-gulo- and -altro-pyranosides.

At the present time, with the limited amount of information available, it is impossible to decide between the various possibilities. It should be noted that, although these results were obtained with glycosides, the arguments are probably applicable to other carbohydrates, since Heyns and Klier[12] and Shafizadeh[13] have found that a wide range of carbohydrates, including phenyl glycosides and cellulose, all give the same fragmentation products.

EXPERIMENTAL

Materials and general methods. — Melting points were determined with a Mel-temp apparatus and are uncorrected. G.l.c. was performed with a Perkin–Elmer Model 900 instrument equipped with flame-ionization detectors. Carbohydrates were separated as *O*-trimethylsilyl derivatives on a stainless steel column (6 ft × 0.125 in.) packed with 5% SE-30 on Chromosorb W. Methanol was analyzed by using a stainless steel column (12 ft. × 0.125 in.) packed with 10% Carbowax 20M on Chromosorb W. Quantitative data were obtained with an Infotronic Model CRS-208 digital integrator.

Methyl α-D-altropyranoside and methyl α-D-gulopyranoside were kindly provided by Dr. N. K. Richtmyer and Mr. E. Zissis. Methyl α-D-glucopyranoside, methyl α-D-galactopyranoside, and methyl α-D-mannopyranoside were obtained commercially and purified by recrystallization from ethanol (see Table I).

Thermal analysis. — The t.g. and d.t.g. data were obtained with a Perkin–Elmer Model TGS-1 thermobalance unit, using 1–2-mg samples in sealed aluminum pans (Perkin–Elmer Sample Sealer Assembly No. 219-0061) containing small holes. The holes allowed the volatile decomposition products to escape, but minimized the amount of evaporation of the glycoside. The dynamic thermal analysis was done at a programmed rate of 10°/min in an atmosphere of nitrogen (40 ml/min). Temperature calibration of the thermal balance was done by using the magnetic curie points of alumel (163°) and nickel (354°). The isothermal kinetic data were obtained from the t.g.a. curves held at 227° ±1.0°. The results are summarized in Table I and Figs. 1 and 2.

Condensation of glycosides. — Samples (1–2 mg) of the glycosides in aluminum pans were heated in the t.g.a. instrument to several different levels of weight-loss. The pans were then placed in small test-tubes and broken open with a microprobe. A weighed amount of D-glucitol (1–2 mg) was added as internal standard. Parts of the samples were silylated by the procedure of Sweeley[15] and analyzed by g.l.c. for starting material and 1,6-anhydro sugar. The remaining material was hydrolyzed with 0.5M hydrochloric acid, following the procedure of Laver and associates[16], and then analyzed by g.l.c. (see Table II).

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