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THERMOLYSIS OF PHENYL β-D-GLUCOPYRANOSIDE CATALYZED BY ZINC CHLORIDE

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ABSTRACT

Thermolysis of phenyl β-D-glucopyranoside in the presence of 5% of zinc chloride proceeds at relatively low temperatures and in two distinct stages. In the first stage, the Lewis acid facilitates nucleophilic displacement of the glycosidic group and formation of randomly linked and branched glucosans. In the second stage, zinc chloride catalyzes elimination of hydroxyl groups and subsequent dehydration of the molecule and charring.

INTRODUCTION

Preceding studies have shown that heating of 1,6-anhydro-β-D-glucopyranose (levoglucosan)[1,2], phenyl glucosides[3–7], disaccharides[8], and cellulose[9] results in the cleavage of the glycosidic bond through a transglycosylation reaction and subsequent decomposition of the sugar units. We now report the catalytic effect of zinc chloride on the pyrolytic reactions of phenyl β-D-glucopyranoside, a compound selected as a model for a study of the pyrolysis and flame-proofing of cellulosic materials[10].

RESULTS AND DISCUSSION

Thermal analysis. — The thermal analysis data for crystalline phenyl β-D-glucopyranoside[5,11] show loss of water of crystallization at 85°, melting at 176°, decomposition peaks at 305 and 330°, and the leaving of 12% of carbonaceous residue at 400°. The α-D anomer behaves in a similar way, but, as water of crystallization is not present, the peak at 85° is absent[6]. As may be seen in Fig. 1, addition of 5% of zinc chloride substantially changes the thermal properties of phenyl β-D-glucopyranoside. In this Figure, differential thermal analysis (d.t.a.), thermogravimetric analysis (t.g.a.), and derivative thermogravimetry (d.t.g.) curves reflect the sequence of physical transformations and chemical reactions as the mixture is heated at a constant rate. The d.t.a. curve shows a broad melting endotherm at ~140°, followed by an exothermic decomposition peak at 220° that is accompanied by a rapid weight-loss, leaving 49% of carbonaceous residue at 400° as indicated by the t.g.a. curve. The d.t.g. curve shows the rate of weight-loss. Again, the α-D anomer behaves very similarly (see Fig. 2).

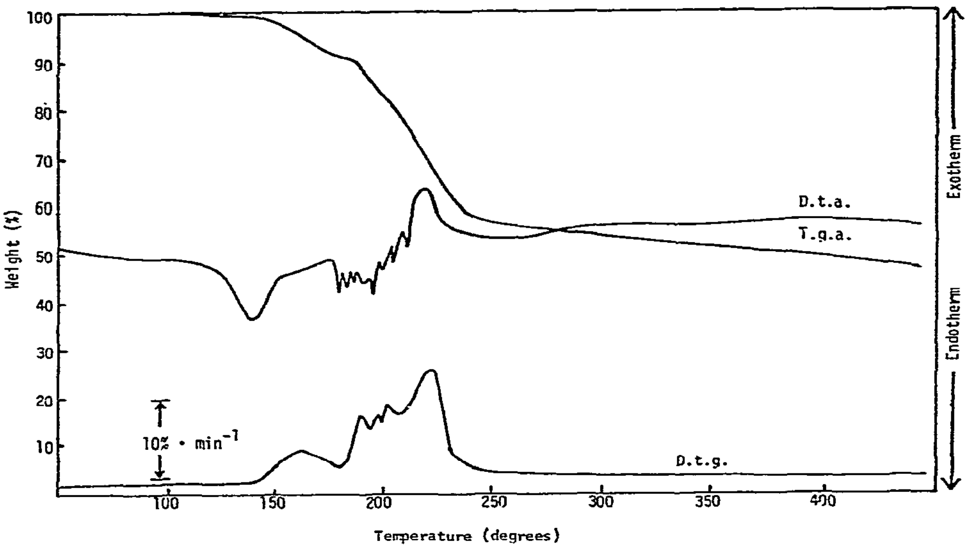

Fig. 1. Thermograms of phenyl β-D-glucopyranoside in the presence of 5% of zinc chloride. [D.t.a. is given on the right-hand scale, t.g.a. on the left-hand scale, and d.t.g. on the scale indicated.].

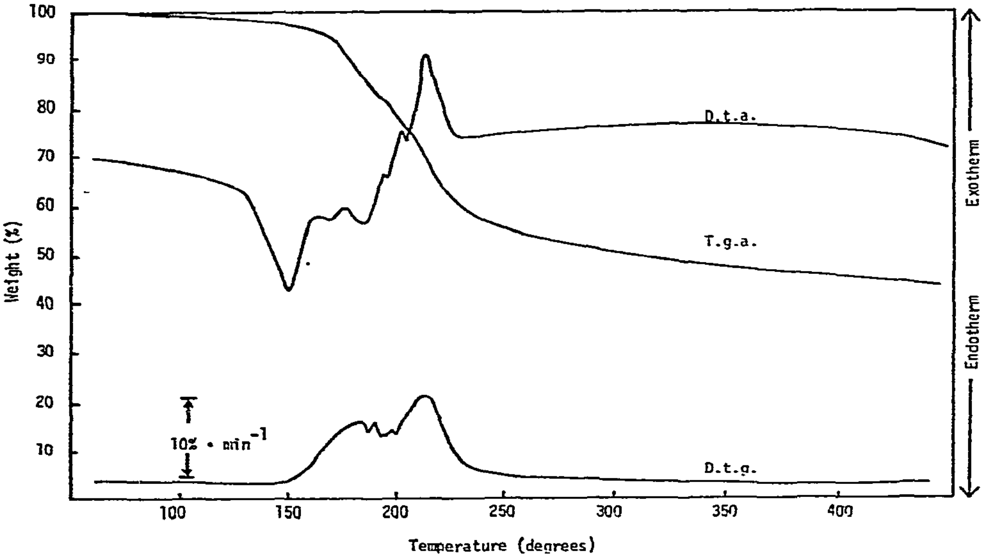

Fig. 2. Thermograms of phenyl α-D-glucopyranoside in the presence of 5% of zinc chloride. [D.t.a. is given on the right-hand scale, t.g.a. on the left-hand scale, and d.t.g. on the scale indicated.]

Cleavage of the D*-glucosidic group.* — In the absence of zinc chloride, the D-glucopyranosides remain almost intact up to the decomposition range of ~300°, when trans-D-glucosylation occurs with quantitative evolution of phenol[5,7], and the sugar moieties decompose shortly afterwards. However, when zinc chloride is added, the trans-D-glucosylation and decomposition reactions proceed at considerably lower temperatures and in two distinct stages. The products formed during the initial stage of thermal events were determined by analysis by gas–liquid chromatography (g.l.c.) of samples heated within the range of 140–155°. The results presented in Table I show that the D-glucosides gradually react in this range to form D-glucosans (condensation products). The reaction mixtures contain small proportions of levoglucosan and the starting materials, but yield almost 90% of D-glucose on hydrolysis with acid.

TABLE I

MONOMERIC PRODUCTS FORMED BY HEATING OF PHENYL α- OR β-D-GLUCOPYRANOSIDE CONTAINING 5% OF ZINC CHLORIDE TO VARIOUS TEMPERATURES

Temperature of sample (degrees)	*Levoglucosan (%)*	D-*Glucopyranose*		*Phenyl* D-*glucopyranoside* (%)		*Glucose after acid hydrolysis* (%)
		α-	*β-*	*α-*	*β-*	
			α-D Anomer			
25	—	—	—	100.0	—	
135	2.8	T[a]	T	90.5	T[a]	
140	4.2	T	T	75.0	T	
145	3.6	T	T	63.2	T	
150	6.8	T	T	47.1	T	
155	4.2	T	T	30.3	T	
165	2.1	T	T	3.1	T	85
			β-D Anomer			
25	—	—	—	—	100.0	
140	6.3	T	T	1.5	80.3	
145	4.2	T	T	1.5	21.0	
150	4.6	T	T	3.0	16.8	
155	3.1	T	T	1.1	6.0	88

[a] T = trace amounts.

The condensation products were examined by fractionation and structural studies. For these investigations, samples of phenyl β-D-glucopyranoside, either neat or containing zinc chloride, were heated at 230° and 135°, respectively. The mixtures were then cooled and washed with methanol, and the residue was fractionated by gel filtration on Sephadex G-25 to give the elution patterns shown in Fig. 3. These data indicated that a polysaccharide (A) and an oligosaccharide fraction (B) were produced under both uncatalyzed and catalyzed conditions. The yields and some of the physical and chemical properties of the products are given in Table II.

TABLE II

PRODUCTS OF THE PYROLYSIS OF PHENYL β-D-GLUCOPYRANOSIDE AT 230° IN THE ABSENCE, AND AT 135° IN THE PRESENCE, OF ZINC CHLORIDE

Fraction	*Neat*				*+5% of $ZnCl_2$*			
	Yield (%)	*Color*	$[\alpha]_D^{25}$ (*degrees*)	*Glucose on acid hydrolysis* (%)	*Yield* (%)	*Color*	$[\alpha]_D^{25}$ (*degrees*)	*Glucose on acid hydrolysis* (%)
Volatile (weight loss)	24[a]				12[a]			
Methanol-soluble	48[a]				74[a]			
Water-soluble	24[a]				14[a]			
A (polysaccharide)	52[b]	black	+105	40.2	61[b]	light-yellow	+75.4	63.5
B (oligosaccharide)	11[b]	brown	+86	51.5	31[b]	cream	+70.0	85.0
C	37[b]	brown			9[b]			
Water-insoluble	4[a]							

[a] Percent of the original sample. [b] Percent of the water-soluble fraction.

TABLE III

END-GROUP DETERMINATION AND PERIODATE OXIDATION OF THE PRODUCTS FROM THE THERMAL CONDENSATION OF PHENYL β-D-GLUCOPYRANOSIDE

Glucosan	*Ratio of glucose to glucitol*	*Periodate consumption*[a]	*Smith-degradation products*[b]					
			Glycerol	*Erythritol*	*Unknown*	*3,6-Anhydroglucose*	*Xylose*	*Glucose*
By heating of the neat β-D-glucoside								
Fraction A	no D-glucitol	1.13	2.5	0.4			<0.1	1
Fraction B	no D-glucitol	1.30	2.6	0.6			<0.1	1
By heating of the β-D-glucoside in the presence of 5% of $ZnCl_2$								
Fraction A	108:1	1.14	1.9	0.1	0.1	T[c]	0.4	1
Fraction B	40:1	1.28	2.4	0.3	0.1	0.1	1.4	1

[a] Molecules of oxidant per D-glucose residue. [b] Molar ratios. [c] T = trace amounts.

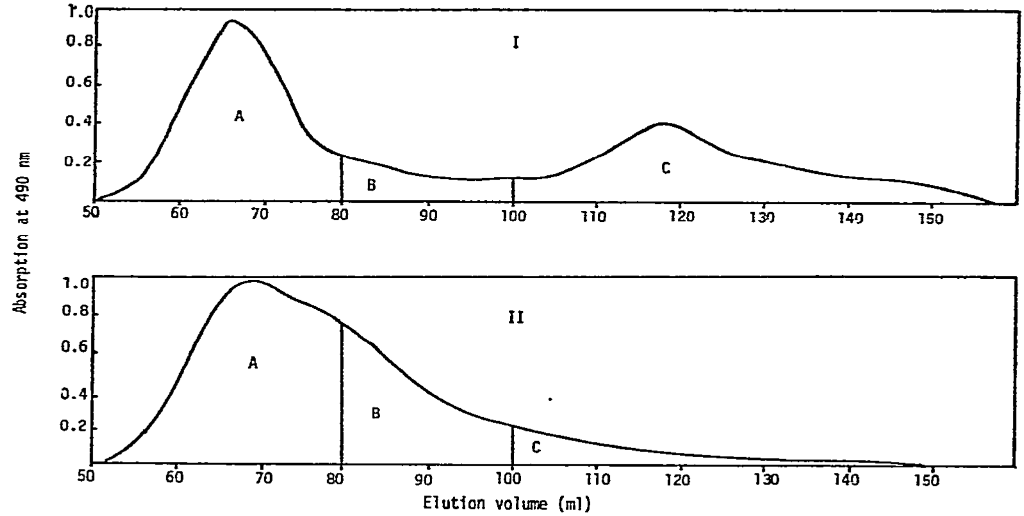

Fig. 3. Gel-filtration pattern of the thermal-polymerization products of phenyl β-D-glucopyranoside in the absence (I) and presence (II) of zinc chloride: A, polysaccharide fraction; B, oligosaccharide fraction; C, disaccharide and monosaccharide fraction.

Acid hydrolysis of the two fractions (A and B) of higher molecular weight derived from the β-D-glucoside under uncatalyzed conditions gave D-glucose only. However, in addition to D-glucose, the corresponding fractions from the β-D-glucoside under catalyzed conditions also gave a trace amount of 3,6-anhydro-D-glucose. Furthermore, the fractions showed an infrared (i.r.) absorption band at 1710 cm^{-1} for carbonyl group, and ultraviolet (u.v.) absorption maxima at 220 and 275 nm. As previously discussed[4,8], dehydration of the sugar moiety accounts for this phenomenon, which is also observed with other thermal polymers.

The specific rotations of the polysaccharides formed under uncatalyzed (+105°) and catalyzed (+75.4°) conditions were similar to those of thermal polymers from cellobiose, α,α-trehalose[8], and synthetic D-glucose polymers[12] having a high content of α-D-glucosidic links.

End-group analysis involving reduction followed by acid hydrolysis gave no D-glucitol for the uncatalyzed condensation-products, and a ratio of 40 to 108:1 of D-glucose to D-glucitol for the catalyzed condensation-products.

Further information on the molecular structure of the polysaccharide and oligosaccharide fractions was obtained by periodate oxidation. Fractions A and B each consumed ~1.2 molecules of periodate per D-glucose residue. There was no significant difference in the proportion of oxidant consumed by the materials prepared under uncatalyzed or catalyzed conditions. After successive periodate oxidation, borohydride reduction, and acid hydrolysis of fractions A and B, g.l.c. analysis showed the presence of D-glucose, D-xylose, glycerol, and erythritol for both types of polymer, as summarized in Table III. In addition to these products, the catalyzed polymer gave small proportions of 3,6-anhydroglucose and two unknown compounds that, as discussed later, proved to be closely related compounds. The relative proportions of these products were similar for various fractions of the uncatalyzed or catalyzed polymer, but were quite different for the two types of polymer. The catalyzed polymer gave a substantial proportion of D-xylose as the Smith-degradation product, whereas the uncatalyzed polymer gave only a small proportion of D-xylose originating from furanoid structures.

These data indicated that the trans-D-glucosylation products are randomly linked, and branched. Also, the "reducing" end-groups are not free, presumably because of anhydro-ring formation, which prevails under the pyrolytic conditions. Addition of zinc chloride facilitates the nucleophilic substitution of the D-glucosidic group, and results in more-drastic transformations, including formation of furanoid and 3,6-anhydride structures.

Kinetic studies. — Thermal cleavage of phenyl D-glucopyranosides catalyzed by zinc chloride was further studied by isothermal, kinetic methods. The thermal reaction was monitored by colorimetric determination of the phenol liberated within the range of 100–130°. The resulting data, as may be seen in Fig. 4, fit the equation ln $c^{-1} = kt$ for pseudo-first-order kinetics, where c is the mole fraction of unreacted D-glucoside after reaction time t, and k is the pseudo-first-order rate-constant. The rate constants (given in Table IV) calculated from the data were, in turn, fitted to the Arrhenius equation by the least-squares method, to give an activation energy of 106.7 kJ.mole^{-1} for the β-D anomer. This value is considerably lower than the activation energies of

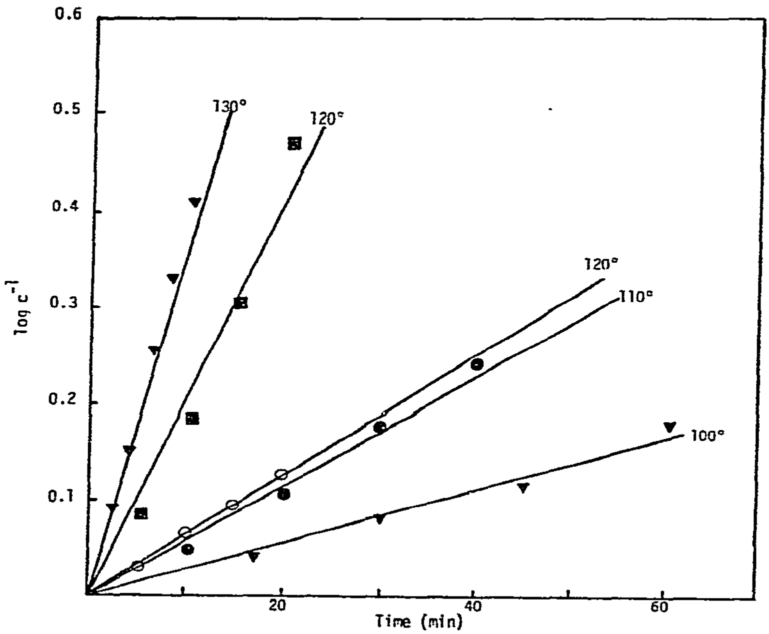

Fig. 4. Rates of isothermal pyrolysis of the phenyl D-glucopyranosides in the presence of 5% of zinc chloride [α Anomer: hollow symbols; β anomer: solid symbols.]

TABLE IV

RATE CONSTANTS OF THE THERMOLYSIS OF PHENYL α- AND β-D-GLUCOPYRANOSIDE CATALYZED BY ZINC CHLORIDE

Temperature (degrees)	k × *10*^{2} *(min*$^{-1}$*)*	
	α-D	β-D
100		0.7
110		1.1
120	1.4	4.6
130		8.5

187.1 and 144.4 kJ.mole^{-1} found for uncatalyzed[5] and alkali-catalyzed[6] conditions, respectively.

The data in Table IV show that, in the presence of zinc chloride, the β-D anomer reacts ~3 times as fast as the α-D anomer. The same order of anomeric reactivity has been observed for pyrolysis under alkaline conditions[6]. However, for hydrolysis by aqueous acid[13], the order is reversed, the α-D anomer being hydrolyzed 4 times as fast as the β-D anomer; this indicates that hydrolysis and pyrolysis proceed by different mechanisms.

Decomposition of the sugar moiety. — Decomposition of the condensation products on further heating was investigated by g.l.c. and by chemical analysis of the products of pyrolysis at 350 and 600°; both temperatures provided similar results, the major products consisting of carbon dioxide, char, tar, and water. The minor volatile products included 2-furaldehyde, 2,3-butanedione, 2-methylfuran, benzofuran, and 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose ("levoglucosenone")[14,15]. The yields obtained at 600° are given in Table V.

After per(trimethylsilyl)ation of the tar fraction before hydrolysis, g.l.c. analysis showed only minor proportions of phenyl glucoside and levoglucosan, but, after acid hydrolysis, ~50% of the tar gave rise to D-glucose, the two unknown sugar derivatives, and 3,6-anhydro-D-glucose. The unknown compounds had the same mobility in thin-layer chromatography (t.l.c.) as 3,6-anhydro-D-glucose, and their g.l.c. peaks were close to and their mass spectra similar to those of this anhydride. They were formed from authentic, crystalline 3,6-anhydro-D-glucose in low yield, either by treatment with pyridine or aqueous acid, indicating that they were probably isomers thereof. The data summarized in Table V showed that the tar is composed mainly of condensation products having glycosidic and ether links. The fact that only 50% of the D-glucose units could be recovered from the tar fraction after hydrolysis with acid indicated that the condensation products in the tar fraction are partially dehydrated and decomposed.

Dehydration and fission are the primary decomposition reactions of the sugar moiety[1,2]. These reactions are respectively promoted by acidic and alkaline catalysts, and lead to further rearrangements and disproportionation of the molecule. Among the volatile products, 2-furaldehyde, 2-methylfuran, and "levoglucosenone" are dehydration products. Benzofuran and 2,3-butanedione are formed by a unique, acid-catalyzed, fission and dehydration reaction of phenyl D-glucopyranosides[15].

TABLE V

PRODUCTS OF THE PYROLYSIS OF PHENYL α- OR β-D-GLUCOPYRANOSIDE IN THE PRESENCE OF ZINC CHLORIDE AT 600°

Product	*Yield* (%)	
	α-	β-
2-Methylfuran	0.7	0.7
2,3-Butanedione	1.1	3.9
2-Furaldehyde	3.6	3.4
Benzofuran	0.4	0.6
"Levoglucosenone"	T	T
Carbon dioxide	6.0	5.1
Water	16.6	15.2
Char	33.5	32.6
Tar	6.8	5.4
Before acid hydrolysis		
levoglucosan	(3.6)[a]	(2.6)
phenyl D-glucopyranosides		
α-	(1.2)	(0.7)
β-		(2.7)
After acid hydrolysis		
glucose	(20.8)	(26.7)
3,6-anhydroglucose	(1.6)	(1.0)
unknown	(12)	(16)

[a] Numbers in parentheses are percentages of the tar fraction.

The data in Table V show that, during the thermal decomposition (the second thermal event in Fig. 1), zinc chloride catalyzes the elimination of hydroxyl groups, and this leads to substantial dehydration and charring, rather than to fission and volatilization of the molecule. At this stage, the catalyst apparently plays another significant role, because the elimination and dehydration should provide furan derivatives and other volatile compounds[1,2]. Formation of substantial proportions of char and water, and only minor proportions of the volatile dehydration products, as well as development of ether links, indicates that zinc chloride not only catalyzes the initial dehydration reaction but also helps to condense the intermediate products to non-volatile materials that are charred on further heating, These data throw considerable light on the mechanisms of charring of carbohydrates, a subject of considerable academic and technological interest[10,16]. Thus, charring of carbohydrates involves dehydration, condensation, and carbonization. The last process involves further elimination of the substituents, development of stable free-radicals[2,5], and formation of new carbon bonds on further heating[10].

EXPERIMENTAL

Preparation of samples. — Phenyl α-D-glucopyranoside was prepared as described previously[17]; the β anomer was obtained from Sigma Chemical Company. A sample of each of these compounds was dissolved in that volume of a solution of zinc chloride in methanol that was calculated to add 5% of the catalyst after evaporation of the solvent; that is, the ratio (w/w) of D-glucoside to zinc chloride was 19:1. These mixtures were dried *in vacuo* below 50°, and stored under anhydrous conditions.

Analytical methods. — The thermal analysis, u.v. spectroscopy, t.l.c., and g.l.c. of carbohydrates were conducted by use of the methods and equipment already described[3–6,8]. Thermal analysis was programmed at the rate of $15°.\mathrm{min}^{-1}$.

Thermolysis of phenyl D-*glucopyranosides.* — Small samples (~2 mg) of the glucosides in the presence of 5% of zinc chloride were heated, at the rate of $15°.\mathrm{min}^{-1}$, in the d.t.a. instrument to temperatures corresponding to the various thermal events. The heated samples were then cooled, per(trimethylsilyl)ated, and the products analyzed by g.l.c. for the ethers of the monomeric compounds levoglucosan, α- and β-D-glucose, and the starting glycosides. The results obtained are given in Table I.

Isolation and investigation of the thermal-condensation products. — The D-glucoside (2 g), either neat or treated with zinc chloride, was placed in a 100-ml flask, which was then flushed with nitrogen, and held for 30 min in an oven at 230 or 135°, respectively. The resulting weight-loss was then recorded, and the residue was washed with methanol. A solution of the solid (0.3 g) in water (5 ml) was chromatographed on a column (1.5 × 125 cm) of Sephadex G-25 at room temperature at a flow rate of $\sim 10\ \mathrm{ml.h}^{-1}$. The eluate was collected in fractions (5–10 ml), and the amount of carbohydrate material in each fraction was determined by the phenol–sulfuric acid method[8], giving the elution pattern shown in Fig. 3. The appropriate fractions were combined into three major fractions, as indicated by the chromatographic pattern, and each was then concentrated to a small volume and freeze-dried. The products were investigated both by physical and chemical methods. The results are recorded in Table II. The data obtained by end-group analysis and by Smith degradation are given in Table III. These determinations were made by the methods previously described[8].

Kinetic experiments. — Small samples (~5 mg) of the D-glucoside containing 5% of zinc chloride were weighed, and each was sealed in an ampoule (5 ml) under a nitrogen atmosphere. The ampoules were then heated in a constant-temperature oil-bath for different periods, rapidly cooled in cold water, and opened. Each reaction mixture was dissolved in distilled water (5 ml), and 1-ml aliquots of the solution were diluted with M sodium hydroxide (10 to 20 ml). The amount of free phenol in each final solution was determined colorimetrically by the u.v. absorption at 287 nm ($\varepsilon_{\mathrm{mM}}$ 2.60), which gave the amount (*c*) of unreacted phenyl D-glucoside, used for calculation of the rates shown in Fig. 4.

Thermal degradation. — Samples (100 mg) of the D-glucoside containing 5% of zinc chloride were heated under nitrogen for 8 min at 600° in a modified, Sargent micro-combustion apparatus. The products were swept through a series of condensers by means of a gentle stream of nitrogen, and fractionally collected downstream from the furnace, giving a tar fraction condensed on the pyrolysis tube, an aqueous pyrolyzate that was collected in a Dry Ice–acetone trap, uncondensed gases, and a residue of char. The uncondensed gases were passed through a solution of barium hydroxide in order to recover the carbon dioxide as barium carbonate.

The tar fraction, before and after acid hydrolysis with M hydrochloric acid at 100°, was analyzed for monomeric products by g.l.c. The results are summarized in Table V.

The reference compound 3,6-anhydro-D-glucose, prepared by hydrolysis of methyl 3,6-anhydro-β-D-glucopyranoside[18], was obtained as crystals, m.p. 117–119° [lit. 117–119° (ref. 18), 120–121° (ref. 19)]. On per(trimethylsilyl)ation of this compound, the ether displayed a major peak and a small shoulder in g.l.c., presumably for the α- and β-D anomers. However, on boiling a solution of the crystals in 0.1M hydrochloric acid for 4 h, two additional peaks appeared that had the respective retention-times corresponding to those of the two unknown compounds. The hydrolyzed solution showed no u.v. absorption, and, in t.l.c., only one component, having an R_F value identical to that of the crystalline compound. The same new g.l.c. peaks appeared after melting or treatment of the crystals with pyridine. Furthermore, g.l.c.–m.s. gave almost identical spectra for the two unknown compounds and 3,6-anhydro-D-glucose.

For direct analysis of the volatile products and water, small samples (5 mg) were pyrolyzed at 350 and 600° in a modified Perkin–Elmer pyrolysis unit connected to a gas chromatograph. The products were resolved by g.l.c., and identified by established methods[1,4,15]. The results are given in Table V.

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