Carbohydrate Research, 29 (1973) 113–122

PYROLYSIS OF CELLULOSE

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(Received November 17th, 1972; accepted for publication, December 6th, 1972)

ABSTRACT

Pyrolysis of cellulose under vacuum and atmospheric pressure gave a tar containing various amounts of 1,6-anhydro-β-D-glucopyranose, 1,6-anhydro-β-D-glucofuranose, α- and β-D-glucose, 3-deoxy-D-*erythro*-hexosulose, oligo- and polysaccharides, and some dehydration products. The polysaccharide fraction had no reducing end-group, was randomly linked, contained some furanoid rings, and was very similar to the polysaccharide condensation-product of 1,6-anhydro-β-D-glucose. These results are consistent with a series of inter- and intra-molecular transglycosylation and dehydration and rehydration reactions.

INTRODUCTION

The pyrolysis of cellulose and cellulosic materials has been investigated under a variety of conditions in relation to problems of fire, chemical utilization, and other technical subjects[1]. These investigations have produced several theories and considerable discussions about the mechanism of the pyrolytic reactions. The main issues in these discussions concern the mechanism of the formation of 1,6-anhydro-β-D-glucopyranose (levoglucosan) and possible relations of this mechanism to further degradation of cellulose under various conditions. The suggested mechanisms[1] include cleavage of the molecule through a homolytic process[2,3], and formation of 1,2-, 1,4-, or 1,6-anhydro sugars which are subsequently rearranged to more-stable compounds or degraded to products of lower molecular weight and char[4–7].

In this laboratory, a combination of physical and chemical methods, including thermal analysis, e.s.r. spectroscopy, isotopic tracing, and chemical analysis of the degradation products, has been used to study the thermal reactions of carbohydrates[8–14]. The results obtained with model compounds provide a new basis for better understanding of the corresponding pyrolytic transformations of cellulose which are discussed in this paper.

RESULTS

The thermogram of cellulose shown in Fig. 1 indicates that the pyrolysis of pure (untreated) material begins at ~300° as an endothermic process (d.t.a.) and, as the

temperature is increased, proceeds very rapidly (t.g.a.), reaching a maximum rate of weight loss at 360° (d.t.g.) and leaving a residue of 12%. In a parallel isothermal experiment, samples of cellulose were heated at 300° in nitrogen currents, under vacuum or atmospheric pressure, and the products were investigated to gain further information about the pyrolysis process. The pyrolysis products consisted of char, a tar fraction, and volatile degradation products.

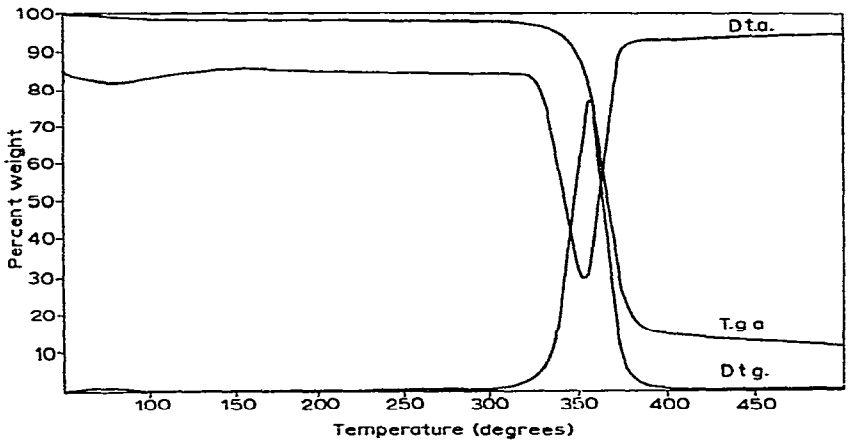


Fig. 1. Thermogram of untreated cellulose.

Trimethylsilylation and g.l.c. of the tar gave a chromatogram (Fig. 2) containing major peaks for 1,6-anhydro-β-D-glucopyranose, 1,6-anhydro-β-D-glucofuranose, 5-(hydroxymethyl)-2-furaldehyde, and two unknown compounds. There were also some minor peaks corresponding to α-D-glucose, β-D-glucose, different tautomeric forms of 3-deoxy-D-*erythro*-hexosulose, and various disaccharides. The presence of the 3-deoxy compound was confirmed by borohydride reduction of the tar and subsequent g.l.c. which gave overlapping peaks for the resulting two 3-deoxy-D-hexitols (Fig. 3).

Further analysis of the tar fraction by t.l.c. of the 2,4-dinitrophenylhydrazone derivatives showed the presence of 3-deoxy-D-*erythro*-hexosulose, 5-(hydroxymethyl)-2-furaldehyde and other degradation products of lower molecular weight, including 2-furyl hydroxymethyl ketone, 5-methyl-2-furaldehyde, 2-furaldehyde, 2,3-butanedione, pyruvaldehyde, glyoxal, and glycolaldehyde, which are partially condensed with the tar fraction[13].

Hydrolysis of the tar and analysis of the hydrolysate showed the presence of substantial amounts of D-glucose, derived from the known monomers (1,6-anhydro-β-D-glucopyranose, 1,6-anhydro-β-D-glucofuranose, and α- and β-D-glucose) as well as the unknown oligosaccharides and other condensed sugar moieties, collectively called hydrolysable materials. Quantitative analysis of D-glucose in the hydrolysate gave the amounts of unknown, hydrolysable materials.

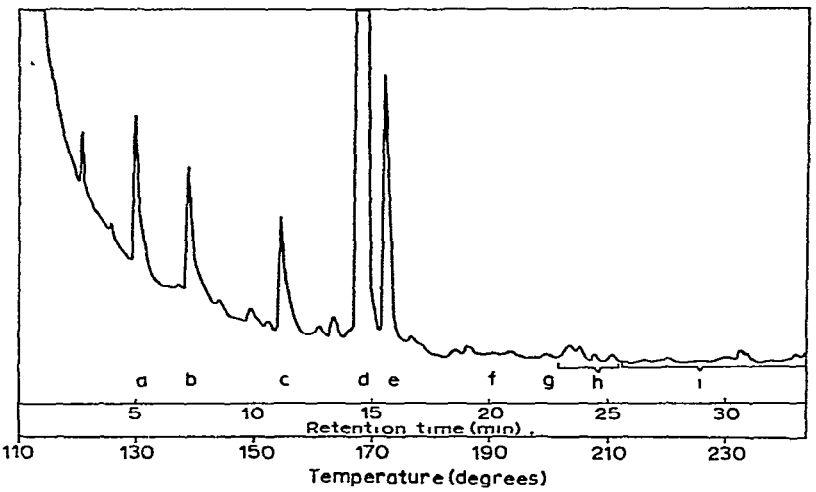


Fig. 2. Chromatogram of cellulose pyrolysis tar: a, 5-(hydroxymethyl)-2-furaldehyde; b and c, unknowns; d, 1,6-anhydro-β-D-glucopyranose; e, 1,6-anhydro-β-D-glucofuranose; f, α-D-glucose; g, β-D-glucose; h, tautomers of 3-deoxy-D-*erythro*-hexosulose; i, oligosaccharide derivatives.

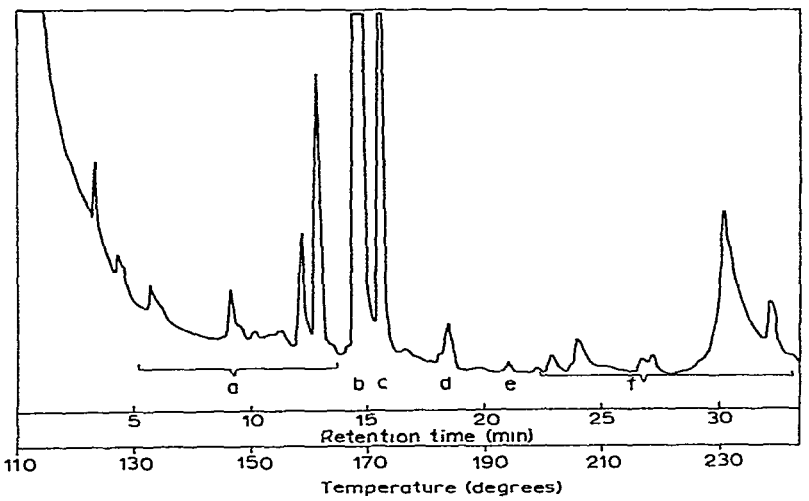


Fig. 3. Chromatogram of cellulose pyrolysis tar after reduction: a, unknown; b, 1,6-anhydro-β-D-glucopyranose; c, 1,6-anhydro-β-D-glucofuranose; d, 3-deoxyhexitols; e, D-glucitol; f, oligosaccharide derivatives.

Table I shows the amounts of char and tar formed at atmospheric pressure or under vacuum, with or without the addition of 5% of antimony trichloride as a Lewis acid catalyst. It also shows the quantitative variation of the major tar components, in terms of the isomeric 1,6-anhydro sugars, D-glucose, and other sugar condensation products (hydrolysables). The thermogram of cellulose treated with antimony tri-

chloride is shown in Fig. 4. This treatment caused gradual dehydration and decomposition of cellulose at relatively low temperatures, leaving more than 40% of char at 400°, and gave very little levoglucosan; sharp pyrolysis of the untreated material at higher temperatures provided a substantial amount of levoglucosan and its condensation products (see Fig. 1 and Table I).

TABLE I

ANALYSIS OF THE PYROLYSIS PRODUCTS OF CELLULOSE AT 300° UNDER NITROGEN

Condition	*Atm. pressure*	*1.5 MmHg*	*1.5 MmHg, 5% of $SbCl_3$*
Char (%)	34.2[a]	17.8[a]	25.8[a]
Tar (%)	19.1	55.8	32.5
Levoglucosan (%)	3.57	28.1	6.68
1,6-Anhydro-β-D-glucofuranose (%)	0.38	5.6	0.91
D-Glucose (%)	trace	trace	2 68
Hydrolysable materials (%)	6.08	20 9	11.8

[a]The percentages are based to the original amount of cellulose.

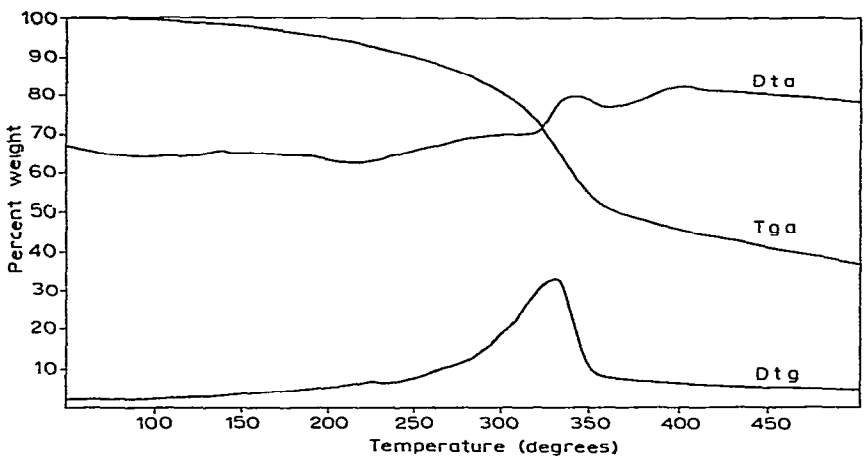


Fig. 4. Thermogram of $SbCl_3$-treated cellulose.

Fractionation by gel permeation of the tar obtained from vacuum pyrolysis of cellulose gave a polymeric product corresponding to 3% of the original cellulose. Hydrolysis of this material gave a quantitative yield of D-glucose. However, end-group analysis, involving reduction with sodium borohydride followed by hydrolysis and g.l.c. analysis, did not show any D-glucitol; D-glucitol would derive from reducing end-groups.

Periodate oxidation of the polymeric material resulted in the reduction of 1.56 moles of the oxidant per D-glucose residue[16]. Reduction of the oxidized material with

sodium borohydride, followed by hydrolysis and g.l.c.[17], gave glycerol, erythritol, D-glucose, and D-xylose, as shown in Table II.

TABLE II

ANALYSIS OF THE POLYMERIC FRACTION OF THE TARS FORM CELLULOSE AND CONDENSATION OF LEVOGLUCOSAN

Source	*Cellulose*	*Levoglucosan*
Total, acid hydrolysis	D-Glucose only	D-Glucose only
End-group analysis	No D-glucitol	No D-glucitol
Periodate consumption (mol.)	1.56	1.45
	Smith-degradation products	
Glycerol	6.4[a]	3.1[a]
Erythritol	1.3	0.5
D-Glucose	1.0	1.0
D-Xylose	0.3	0.6

[a]Relative ratios.

Similar results were obtained from a material produced by uncatalysed polymerization of levoglucosan at 230° and gel permeation of the products (see Table II). Furthermore, the tar fractions of higher molecular weight obtained from pyrolysis of cellulose and polymerization of levoglucosan both displayed closely similar i.r. spectra.

DISCUSSION

Until recently, little information was available about the nature and mechanism of pyrolytic reactions. Consequently, attempts to explain the mechanism of the pyrolysis of cellulose were based on analogy with the transformation of carbohydrate compounds at normal temperatures, often in aqueous solution. Under normal conditions, chemical reactions proceed through a minimum energy pathway, and the solvent plays a significant role in transferring the ionic charges and promoting intermolecular interactions. These types of interaction generally produce a dominant product and are accounted for by a single mechanism. Recent investigation of model compounds, however, has shown that pyrolytic reactions may produce a variety of products through concurrent and consecutive reactions. Furthermore, each product may be derived by different pathways[12,13]. In other words, at high temperatures, when energy barriers are removed, a variety of molecular rearrangements and transformations may take place simultaneously. The recognition and consideration of the differences between normal and pyrolytic reactions leads to a better understanding of the pyrolysis of cellulose and the transformations of the products.

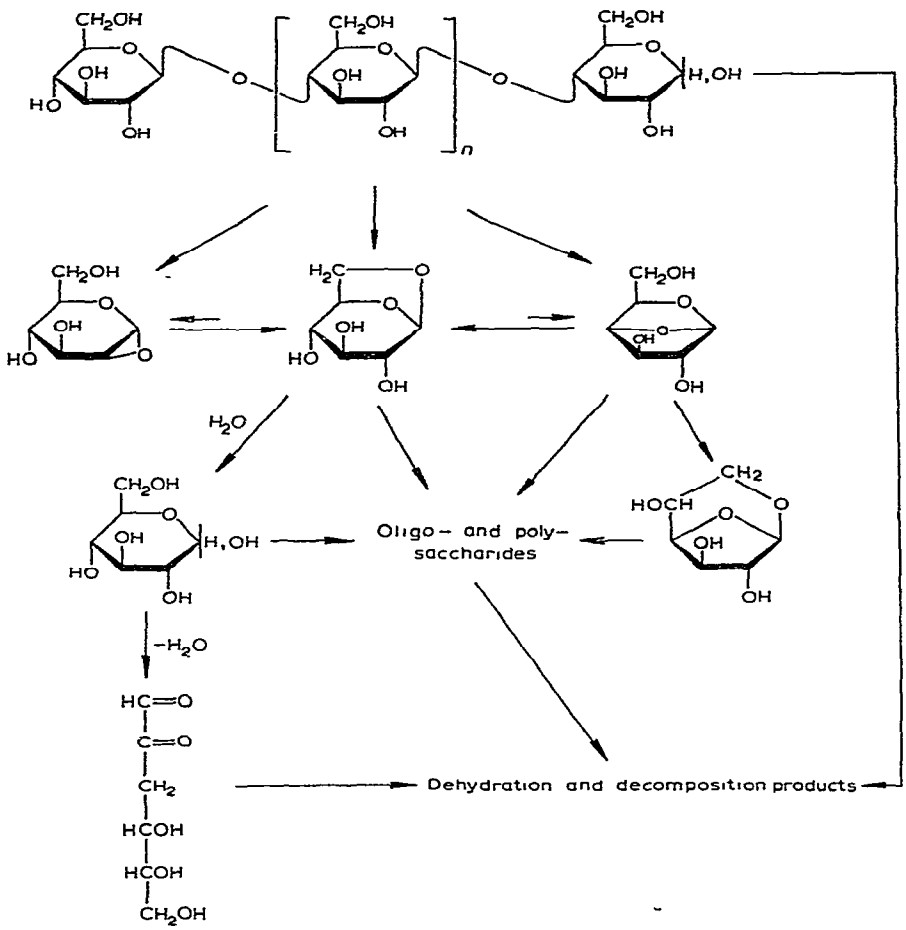
Theoretically, pyrolytic degradation of the cellulose molecule may take place through cleavage of the glycosidic group or dehydration and breakdown of the "anhydroglucose" units. At lower temperatures, some dehydration, elimination, and breakdown of the sugar molecule takes place, resulting in gradual charring and

depolymerization of the molecule[1]. As seen in Fig. 1, these reactions take place very slowly until ~300°, when sufficient energy becomes available for a rapid cleavage of the glycosidic bond and evaporation of the products. This is shown by a large endotherm in d.t.a., a rapid weight-loss in t.g.a., and the formation of levoglucosan and other tarry pyrolysis products (Table I). In contrast to the sharp pyrolysis of pure cellulose, addition of antimony trichloride, as shown in Fig. 4, promotes the decomposition of the molecule over an extended temperature range. As already shown, for the thermal degradation of levoglucosan[13], phenyl β-D-xylopyranosides[9], and xylan[10], the catalysed decomposition at lower temperatures results in dehydration, charring, and the formation of less levoglucosan and related condensation products.

Cleavage of the glycosidic bond could proceed through a homolytic[1–3] or a heterolytic process[1,4–7]. The homolytic process has been suggested on the basis of the free radicals detected by e.s.r. spectroscopy of the pyrolysis products. However, investigation of model compounds has shown that the free radicals are associated with the char which is produced by the dehydration and degradation of the sugar units[11]. These free radicals are longer lived than the expected, transient free radicals leading to the formation of anydro sugars. Furthermore, it has been shown that the cleavage of glycosidic groups proceeds through a transglycosylation mechanism with the participation of one of the free hydroxyl-groups[9,11,14].

Theoretically, HO-2, -3 or -6 could participate in an intramolecular transglycosylation to break the (1→4)-polymeric link. This reaction will produce a new end-group with HO-4 unblocked which, in turn, may participate in further transglycosylation and propagation of the pyrolysis process. Thus, levoglucosan may be formed directly from cellulose or indirectly through the intermediate formation of 1,2- or 1,4-anhydro-α-D-glucopyranose compounds as shown in Scheme 1. Detection of 1,6-anhydro-β-D-glucofuranose along with 1,6-anhydro-β-D-glucopyranose may be considered as *prima facie* evidence for the intermediate formation of 1,4-anhydro-α-D-glucopyranose which could generate the two 1,6-anhydro sugars[6]. Since the pyrolytic reactions can proceed through alternative pathways, the 1,4-reaction does not exclude the simultaneous, direct participation of HO-6. Neither does it exclude the intermediate formation of 1,2-anhydro-α-D-glucopyranose; although it has been shown that when HO-2 of cellulose is methylated, the pyrolysis still proceeds with formation of levoglucosan 2-methyl ether[18].

The fate of the anhydro sugars which are formed from the cleavage of the glycosidic linkage in cellulose depends on the relative stability of the compound and the prevailing conditions. The 1,2- and 1,4-anhydro sugars are easily converted into the more stable 1,6-anhydro sugars. Under high vacuum, the anhydro sugars are readily removed from the heated reaction zone before extensive degradation and decomposition of the sugar units. Consequently, the tar fraction of the evaporation products contains a mixture of 1,6-anhydro-β-D-glucopyranose, 1,6-anhydro-β-D-glucofuranose, and their further condensation products, consisting of various oligo- and polysaccharides. Partial decomposition and dehydration of these compounds forms 3-deoxy-D-*erythro*-hexosulose, various furan compounds, and aldehydes, as shown



Scheme 1. Pyrolysis of cellulose and transformation of the products.

for the decomposition of levoglucosan[12,13]. Conversely, their hydrolysis forms α- and β-D-glucose which is detected in trace amounts. More free-sugar is formed when antimony trichloride is added (see Table I) because it generates water by dehydration reactions and as a Lewis acid promotes the hydrolysis of glycosidic bonds. Pyrolysis under atmospheric pressure, however, limits the evaporation and removal of anhydro sugars from the heated zone; consequently, the molecular interactions continue until a higher proportion of the sugar moiety is decomposed to char and degradation products of lower molecular weight.

The small peaks in the oligosaccharide region of the tar chromatogram (Fig. 2) showed the random nature of the condensation products, which must have been formed from the anhydro sugars after pyrolysis of cellulose and evaporation of the sugar units. Formation of the polymeric components of the tar from the anhydro sugars, as postulated in Scheme 1, is supported by investigation of the polysaccharide

component of the tars of high molecular weight produced from pyrolysis of cellulose and thermal polymerization of levoglucosan. Hydrolysis of both of these polymeric materials gave a quantitative yield of D-glucose before and after reduction with sodium borohydride. A similar end-group analysis of the polymeric tar obtained from pyrolysis of xylan and methyl β-D-xylopyranoside gave ratios of xylitol to D-xylose[10] of ~1:6. The absence of D-glucitol in the hydrolysate of the reduced polymers from levoglucosan and cellulose tars indicated the presence of a 1,6-anhydro ring structure at the terminal groups.

The periodate oxidation and Smith degradation of the polymeric tar (Table II) showed random linkage and branching at C-2, C-4, and C-3, respectively. Furthermore, isolation of small amounts of D-xylose after Smith degradation indicated that some of the D-glucose residues have a furanoid ring structure and must have been derived from 1,6-anhydro-β-D-glucofuranose or its precursor, 1,4-anhydro-α-D-glucopyranose. Apparently, under the pyrolityc conditions, 1,6-anhydro-β-D-glucopyranose and 1,4-anhydro-α-D-glucopyranose are interconvertible because D-xylose was also found among the Smith-degradation products of the levoglucosan polymer.

Pyrolysis of cellulose at higher temperatures results in further degradation of the D-glucose residues to products of lower molecular weight that will be discussed in a subsequent communication.

EXPERIMENTAL

Pyrolysis of cellulose. — Whatman chromatographic cellulose powder (CF 11) containing less than 0.015% of ash was dried over silica gel in a vacuum desiccator and used in pyrolysis experiments. The dried cellulose sample had a residual moisture content of 2.3% as determined by t.g.a.

The pyrolysis apparatus consisted of a Pyrex tube partly covered by a furnace which was controlled by a Thermac series 6000, Model D30 micro-controller. The pyrolysis tube was swept by a gentle stream of nitrogen adjusted through a regulator and maintained at a pressure of 1.5 mmHg with a high vacuum pump.

A porcelain pyrolysis boat containing 3 g of the cellulose sample was placed in the pyrolysis tube behind a glass-covered magnet and heated at about 100° for 2 h to remove the residual moisture. It was then moved with the magnet to the heated zone within the furnace and pyrolysed at 300° for 2.5 h. The tar fraction condensed on the cooler parts of the pyrolysis tube, and was washed with water, filtered, and freeze-dried. The char remaining in the boat was cooled to room temperature and weighed.

G.l.c. of the tar fraction. — The freeze-dried tar was trimethylsilylated and analysed with a Varian Model 1800 g.l.c. equipped with hydrogen flame detectors and stainless columns (8 ft × 0.125 in.) packed with 3% SE-52 silicone gum supported on Chromosorb W (80–100 mesh.) The g.l.c. peaks were identified by retention time, and by addition of known compounds to the mixture. The quantitative determination of the sugar derivatives was carried out by using D-glucitol as an internal calibration standard.

*Reduction of the tar and 3-deoxy-*D-erythro-*hexosulose.* — Cellulose tar (50 mg) was dissolved in 20 ml of water, and 50 mg of sodium borohydride were added. The reaction mixture was stirred for 2 h at room temperature, treated with Amberlite IR-120(H^+) resin, and then filtered. The filtrate was evaporated under reduced pressure. The boric acid in the residue was removed by repeated addition of methanol and evaporation under reduced pressure. The remaining syrup was dried over phosphorus pentaoxide in a vacuum desiccator.

The reduction of 3-deoxy-D-*erythro*-hexosulose[15] was carried out in the same manner, and the products were analyzed by g.l.c.

T.l.c. of the tar fraction. — The aqueous tar solution (10 ml) was treated with 10 ml of a saturated solution of 2,4-dinitrophenylhydrazine in 2M hydrochloric acid for 12 h at room temperature. The resulting precipitate was filtered off, washed with M hydrochloric acid and water, and dried. The derivatives were analyzed by t.l.c., using silica gel (IB-F Baker-flex) and alumina (Eastman chromatogram) plates, and benzene–tetrahydrofuran and toluene–ethyl acetate mixtures as eluents. The carbonyl compounds were identified by comparison with known compounds and by color development with ethanolamine[19].

Hydrolysis of the tar. — A sample of the tar (8 mg) with the internal standard (D-glucitol) was hydrolysed with 2 ml of M hydrochloric acid for 5 h at 100°. The solution was neutralized with Amberlite IR-45 resin and analysed as before. The results in Table I represent the average of three experiments.

Fractionation of the tar polysaccharides. — The aqueous solution of the tar was charged on a column (4 × 25 cm) of Sephadex G-10 and eluted with water at the rate of 60 ml/h, and the eluted aliquots (25 ml) were concentrated and analysed by t.l.c. The fractions which showed no movement on the t.l.c. plate were combined and freeze-dried.

*Thermal polymerization of 1,6-anhydro-β-*D-*glucopyranose.* — A sample of the anhydro sugar (1 g) was dried and heated under nitrogen for 3 h at 230°. The product was dissolved in water, and the solution was filtered, concentrated, and fractionated as above to isolate the polymeric components.

Periodate oxidation. — The polysaccharide fraction of the cellulose tar (6–9 mg) was dissolved in 15mM sodium periodate (10 ml), and the oxidation was allowed to proceed at room temperature in the dark. The reaction was followed by periodic withdrawals of 0.5-ml aliquots which were diluted to 100 ml with water and analysed by the u.v. absorption[16]. After 5 days, the periodate consumption reached a constant value. The oxidation products were determined by the standard method[17]. Periodate consumption of the polysaccharide fraction obtained from thermal polymerization of 1,6-anhydro-β-D-glucose (6.234 mg) was carried out similarly.

Thermal analysis. — The d.t.a., t.g a., and d.t.g. data were obtained as before[11].

ACKNOWLEDGMENTS

The authors are grateful to the U.S. Environmental Protection Agency, Solid Waste Research Division, for grant No. R800652, and the National Science Founda-

tion, RANN Program for grant No. GI-33645X in support of this work. They also thank Dr. R. A. Susott for the thermal-analysis experiments, Dr. R. Rowell for a sample of 3-deoxy-D-*erythro*-hexosulose, and Dr. F. D. Mills for a sample of 1,6-anhydro-β-D-glucofuranose triacetate.

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