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THERMAL ANALYSIS OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE

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ABSTRACT

Thermal analysis of 1,6-anhydro-β-D-glucopyranose indicates the physical transformations of the molecule, including solid-state transition, melting, and evaporation, as well as the ensuing chemical changes involving polymerization and degradation reactions. Furthermore, modification of these properties could be readily detected by variation of the thermograms. This is shown by the addition of zinc chloride and sodium hydroxide. The presence of zinc chloride promotes dehydration and charring, whereas sodium hydroxide enhances fragmentation of the molecule.

INTRODUCTION

Vacuum pyrolysis of cellulose and starch provides 1,6-anhydro-β-D-glucopyranose[1,2] which, on further heating, could degrade to compounds of low molecular weight[3,4] or recombine to form polymeric materials[5–7]. It is generally assumed that 1,6-anhydro-β-D-glucopyranose is an intermediate product in the thermal degradation of the above polysaccharides[1]. This assumption was confirmed by the observation of Glassner and Pierce[3], who obtained identical products from the pyrolysis of the anhydro sugar and cellulose at the temperature range of 242–360°. Heyns and Klier[4], however, recently found that a number of carbohydrate compounds including monosaccharides, disaccharides, amylopectin, and cellulose, on pyrolysis at 300 to 500°, gave the same volatile, degradation products. This led them to assume that decomposition of these compounds involves similar polymeric intermediates which undergo secondary degradation. Furthermore, since the pyrolysis of the 1,6-anhydrohexoses gave different products, they concluded that anhydro sugars have no special significance in the thermal conversion of the above carbohydrate materials into volatile products or into the polymeric intermediate compounds. It was also found that addition of acidic salts to the mono-, oligo-, and poly-saccharides facilitates the formation of furan compounds, whereas basic salts increase the amount of acyclic carbonyl products.

In spite of the controversy about the significance of 1,6-anhydro-β-D-glucopyranose as an intermediate product of thermal degradation, this compound has been

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selected as a model to demonstrate the unique features of thermal analysis and to gain a better understanding of the complex pyrolytic reaction of the carbohydrate compounds. As shown in the previous papers[1,8], these reactions are of special interest and significance in relation to problems of fire, solid-waste disposal, and pollution.

RESULTS AND DISCUSSION

The combination of differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.) of 1,6-anhydro-β-D-glucopyranose shown in Fig. 1 provides a comprehensive and continuous picture of several consecutive and concurrent physical changes and chemical reactions, which take place when the anhydro sugar is heated. The major endothermic peak at 113° indicates the solid-state transition of the compound into the plastic crystalline phase discussed in previous communications[9,10]. This is followed by a minor endotherm at 180° caused by the melting of the sugar. After the melting point, the t.g.a. curve indicates a weight loss that continues up to 350°, when a relatively stable residue of ~5% is left. At ~280°, there is an inflection in the t.g.a. curve and a sharp exotherm in the d.t.a. curve. Furthermore, the exotherm has a wavy line which is an indication of foaming.

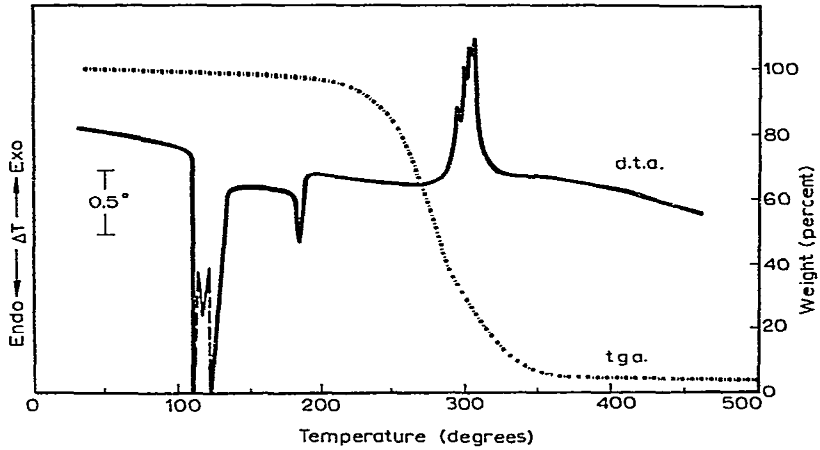
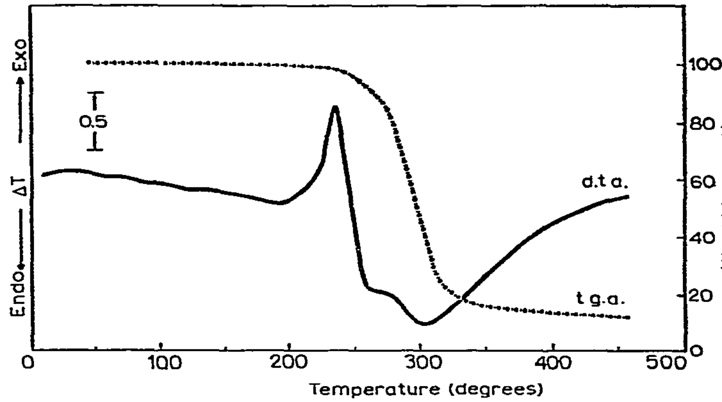


Fig. 1. Thermogram of 1,6-anhydro-β-D-glucopyranose.

Within the temperature range of 180–350°; two different processes account for the weight loss of 1,6-anhydro-β-D-glucose. In the initial stage (180–260°), the weight loss is mainly due to evaporation of the compound which could be simulated by parallel isothermal experiments. At higher temperatures, however, as shown by several isothermal investigations[5–7] (temperature range of 230–240°), the 1,6-anhydro-β-D-glucopyranose is polymerized and the polymer is decomposed[5–7]. In the dynamic thermal analysis, the occurrences of these reactions are signalled by a change in rate of weight loss or the inflection of the t.g.a. line and the appearance of an exotherm in the d.t.a. cruve. The thermogram of the isolated polymerization product (see Fig. 2) shows a rapid weight-loss in the temperature range of 250–350°

which is accompanied by an endothermic reaction. Further condensation gives an initial exotherm, but there are none of the other features seen in the thermogram of the anhydro sugar (Fig. 1). This confirms the assignment of the exotherm to polymerization of levoglucosan.



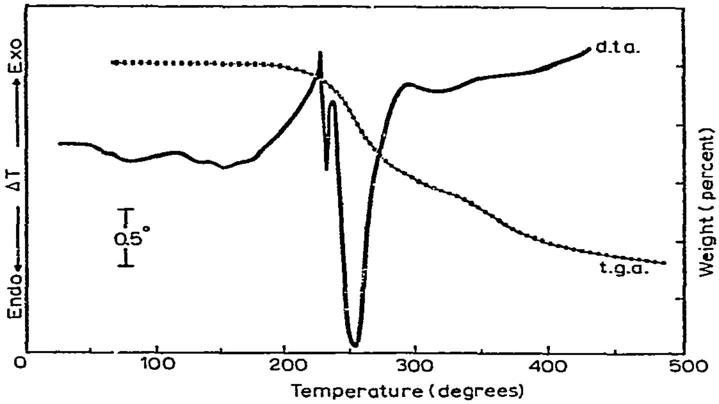


Fig. 2a. Thermogram of uncatalyzed polymerization products of 1,6-anhydro-β-D-glucopyranose.

Fig. 2b. Thermogram of zinc chloride-catalyzed polymerization product of 1,6-anhydro-β-D-glucopyranose.

Modifications of the physical properties and pyrolytic reactions, through the introduction of additives and catalysts, are readily detected by variation of the thermogram. It is known^{6,7} that addition of zinc chloride facilitates or shifts the polymerization of 1,6-anhydro-β-D-glucopyranose to a lower temperature of about 120°. In the dynamic thermal analysis, this phenomenon is evidenced by the appearance of an exothermic peak in the temperature range of 120–180°, following the solid-phase transition endotherm which remains unchanged (see Fig. 3). The polymeric materials that are formed could not escape by distillation at higher temperature. They are slowly degraded by dehydration and charring, leaving a large carbonaceous residue of ~40% at 500°. This is seen from the gradual weight loss, recorded by the t.g.a. curve in the temperature range of 170 to 500°.

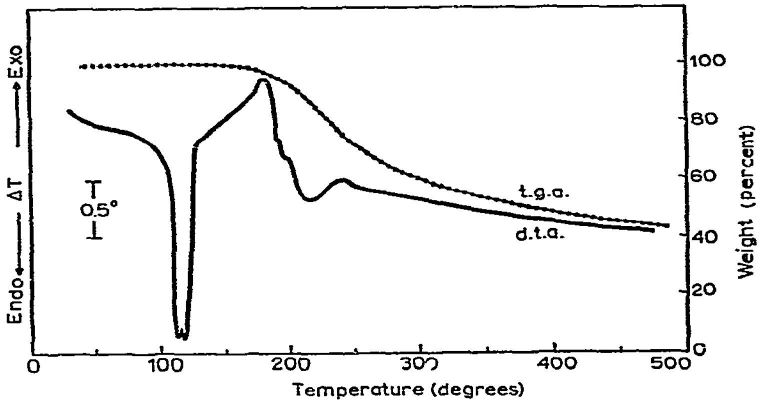


Fig. 3. Thermogram of 1,6-anhydro-β-D-glucopyranose treated with zinc chloride.

Fig. 4 shows that addition of sodium hydroxide results in development of exothermic reactions and volatilization of the molecule, with foaming and frothing, within the temperature range of 175–325°, leaving a residue of ~16%.

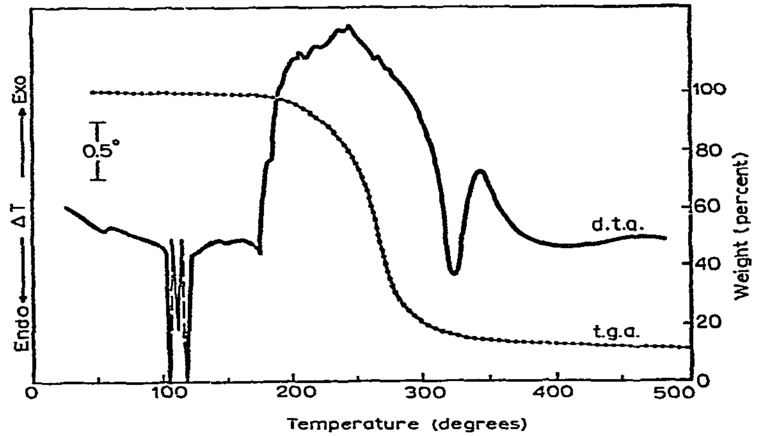
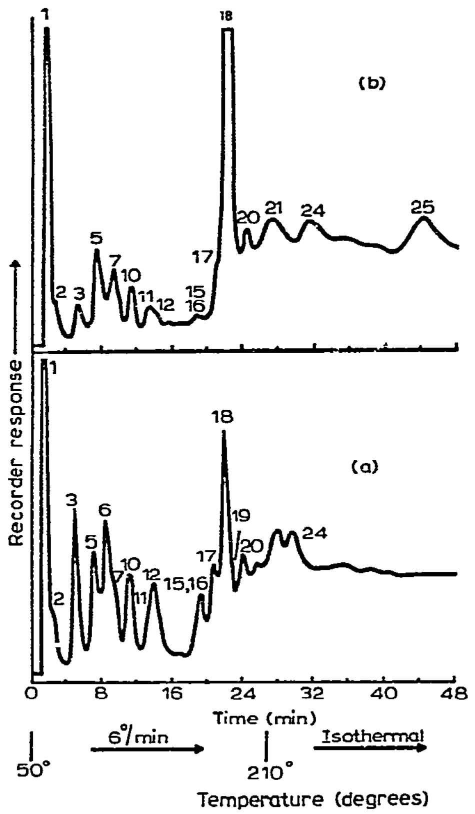


Fig. 4. Thermogram of 1,6-anhydro-β-D-glucopyranose treated with sodium hydroxide.

The nature of the pyrolytic reactions and the difference between the uncatalyzed and the acid- and alkali-catalyzed decomposition of 1,6-anhydro-β-D-glucopyranose could be investigated by the analysis of the decomposition products obtained under isothermal conditions. These products, other than char, water, and tarry materials, include a variety of volatile organic compounds that can be resolved by g.l.c. Figs. 5 and 6 provide a comparison between the chromatograms of the pyrolysis products of the sugar as such, and after the addition of zinc chloride and sodium hydroxide. The major peaks in these chromatograms have been identified by several techniques, including the conversion of the carbonyl compounds into the 2,4-dinitrophenylhydrazone derivatives and t.l.c. of the products.



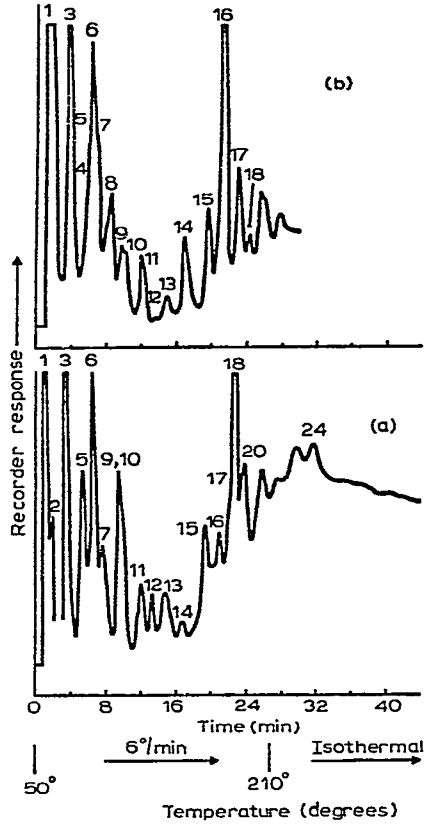


Fig. 5 (left). Chromatograms of the pyrolysis products of 1,6-anhydro-β-D-glucopyranose, before (*a*) and after (*b*) treatment with zinc chloride, obtained under identical experimental conditions.

Fig. 6 (right). Chromatograms of the pyrolysis products of 1,6-anhydro-β-D-glucopyranose, before (*a*) and after (*b*) treatment with sodium hydroxide, obtained under identical experimental conditions.

Table I provides a list of the major pyrolysis products, the method of identification, and the yields obtained under different conditions. These data show that the catalysts used enhance decomposition of the substrate to the final pyrolysis products. Furthermore, addition of zinc chloride results in the increased formation of char, water, carbon dioxide, and 2-furaldehyde which are the expected products of an acid-catalyzed dehydration reaction[1], whereas the addition of alkali promotes the formation of carbonyl compounds of low molecular weight, especially acetaldehyde, glyoxal, 2-butenal, acrylaldehyde, 2,3-butanedione, and carbon dioxide. The formation of these compounds may be accounted for by the base-catalyzed rearrangement and fragmentation reactions of the carbohydrates[11]. The glycosidic bond of 1,6-anhydro-β-D-glucopyranose, which is stable towards alkali at the lower temperatures, may be opened at the elevated temperatures as shown for the alkaline hydrolysis of the glycosides[12]. The sugar molecule could then be degraded through the alkaline reactions which involve enolization, reverse aldolization, elimination, and disproportionation. The d.t.a. curve in Fig. 4 shows that these reactions balance on the exothermic side. In the aqueous, alkaline degradation of sugars, the products may include formaldehyde and aldopentoses, or glyoxal plus aldotetroses, as well as the dominant three-carbon fragments which are converted into lactic acid[11]. As expected under the pyrolytic conditions, the products could be further randomized and changed through subsequent, additional reactions such as decarboxylation. Acetaldehyde, which is the major carbonyl compound formed under the alkaline degradation condition, may have been derived in this manner from such intermediate compounds as lactic acid and pyruvic acid. This was verified through parallel experiments with lactic and pyruvic acids which were found to produce acetaldehyde as the major pyrolysis product.

TABLE I

PYROLYSIS PRODUCTS OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE AND ITS THERMAL POLYMERS

Number	*Compound*	*Anhydro sugar (%)*			*Thermal polymers (%)*		*Identification method*
		Neat	*+ZnCl$_2$*	*+NaOH*	*A*[a]	*B*[b]	
3[c]	Acetaldehyde	1.1	0.3	7.3	1.5	1.2	*1,5,6,7,8*[d]
5	Furan	1.0	1.3	1.6	3.0	3.9	*1,5*
6	Acrylaldehyde	1.7	<0.1	2.6	1.9	1.3	*1,9*
7	Methanol	0.3	0.4	0.7	0.6	0.9	*1,5,6,9*
10	2,3-Butanedione	0.5	0.8	1.6	—	—	*1,4,5,8*
11	2-Butenal	0.7	0.2	2.2	1.1	1.3	*1,4,5,6,8*
15	1-Hydroxy-2-propanone	0.8	<0.1	1.1	—	—	*1,5*
16	Glyoxal	1.4	<0.1	4.9	4.2	2.0	*1,5,6*
17	Acetic acid	1.7	0.7	1.5	1.4	1.4	*1,2,10*
18	2-Furaldehyde	0.9	3.0	0.4	1.3	3.1	*1,2,3,4,5,6*
20	5-Methyl-2-furaldehyde	0.1	0.3	—	0.4	1.0	*1,5*
	Carbon dioxide	2.9	6.8	5.7	8.0	9.2	
	Water	8.7	20.1	14.1	15.2	21.5	
	Char	3.9	29.0	16.0	10.0	26.0	

[a]Polymerized without catalyst. [b]Polymerized with zinc chloride as catalyst. [c]The number refers to the peaks in the chromatogram (Figs. 5 and 6; peaks 1 and 2 are uncondensed gases). [d]The numbers refer to identification methods described in the experimental. [e]The balance is assumed to be mainly tar that includes the evaporated levoglucosan and could not be directly measured under the experimental conditions.

As seen in Table I, the uncatalyzed thermal degradation of 1,6-anhydro-β-D-glucopyranose provides the same products that are obtained from acid- or alkali-catalyzed reactions, but in different amounts. The enhanced formation of these products under either acid or alkaline conditions, and the close similarity with other acid- and alkali-catalyzed reactions of carbohydrates, may be considered as *prima* *facie* evidence for an ionic reaction mechanism[1,13] rather than a homolytic cleavage[1,14]. The ionic reactions also account for the polymerization of levoglucosan that has been investigated in some detail[7].

The thermograms (Figs. 2a, b) indicate a difference between the uncatalyzed and zinc chloride-catalyzed polymerization products. The difference is also seen in Fig. 7 which shows the chromatograms of the pyrolysis products of the two products. Comparison of Fig. 7 with Figs. 5 and 6 shows that the pyrolysis products of levoglucosan and its polymers are qualitatively the same but quantitatively different. This indicates that some of the anhydro sugar could have been pyrolyzed directly.

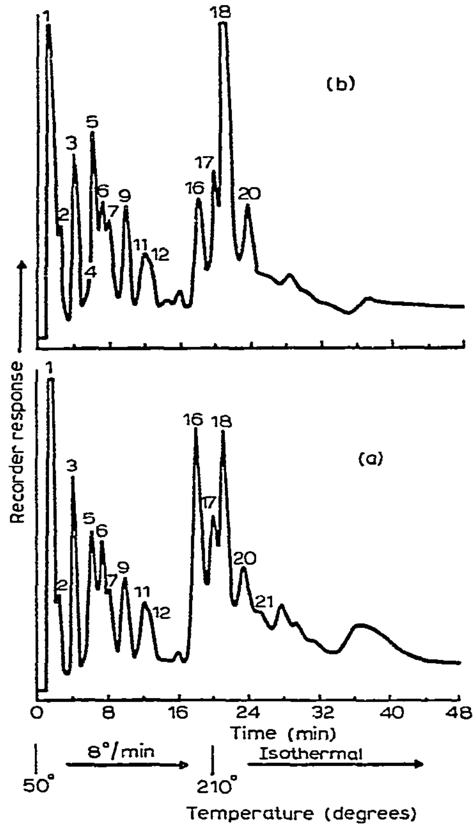


Fig. 7. Chromatograms of the pyrolysis products of the (a) uncatalyzed and (b) zinc chloride-catalyzed polymers of 1,6-anhydro-β-D-glucopyranose.

As in the case of ionizing radiation, the ionic degradation products could form free radicals which may be detected by e.s.r. spectroscopy[15,16]. Further investigation of this subject and its relation to the thermal degradation of cellulose will be reported in a subsequent communication.

EXPERIMENTAL

Preparation of samples. — Crystalline 1,6-anhydro-β-D-glucopyranose (m.p. 180°) was ground in a mortar with or without the additives which consisted of 5% of anhydrous zinc chloride or sodium hydroxide. A minimal amount of tetrahydrofuran was added to dissolve the additive and assure uniform distribution. The solvent was removed under vacuum at 50°, and the dried material was kept under anhydrous conditions.

Samples of the uncatalyzed and zinc chloride-catalyzed polymers of 1,6-anhydro-β-D-glucopyranose were prepared according to the previously reported methods[5,6]. The anhydro sugar was heated at 250° and 150°, and the products were purified by precipitation from an aqueous solution with ethanol. The precipitate was dried under vacuum at 50° for 8 h, powdered, and kept as before.

Dynamic thermal analysis. — The d.t.a. and t.g.a. data were obtained with a DuPont model 950-900 thermal analyzer, programmed at the rate of 15°/min. The experiments were conducted in a nitrogen atmosphere, using silica beads as the reference and 10 mg of the powdered samples. For the t.g.a. experiments, the gas flow was regulated at the rate of 100 ml/min.

Gas–liquid chromatagraphy. — About 12–20 mg of the powdered samples were placed in a small aluminum boat and pyrolyzed at 600° in a Perkin–Elmer pyrolysis unit connected to a Hewlett–Packard F & M model 5750, temperature-programmed, dual-column, g.l.c. instrument.

The connections were modified to allow the carrier gas to bypass the pyrolysis unit or sweep the pyrolysis products directly into the instrument. The volatile pyrolysis products were resolved by using essentially the previously reported conditions[17] with minor modifications. The columns consisted of stainless steel (12 ft × 0.25 in.) packed with Fluoropak 80 coated with 10% of 20M Carbowax. The carrier gas was helium flowing at 45 ml/min for the thermal conductivity measurements and nitrogen at 60 ml/min for flame ionization. The column temperature was programmed between 50 to 210° at the rate of 2 to 8°/min. The flame-ionization detector was sufficiently sensitive so that a 20:1 splitter could be used for collecting a major portion of the individual peaks for chemical identifications. The following methods were used for this purpose: (*1*) comparison of the R_F values and addition of known compounds, (*2*) mass spectroscopy of the side stream collected in a capillary tube cooled with liquid nitrogen, (*3*) u.v. spectroscopy of the collected material, (*4*) bubbling of the side stream in a solution of 2,4-dinitrophenylhydrazone (DNPH) derivatives, (*5*) t.l.c. of the DNPH compounds[18], (*6*) m.p. of the DNPH derivatives, (*7*) i.r. spectrum of these materials, (*8*) Schiff's color test for aldehydes, (*9*) permanganate oxidation of alcohols and t.l.c of the DNPH derivative of the resulting aldehyde, and (*10*) pH test for acids.

Despite a previous report[3], the presence of formaldehyde could not be established, and peak 2 assigned to this material gave negative tests with morphine sulphate and the above methods (*4* and *9*).

Quantitative analysis. — The g.l.c. detector was directly connected to a recorder and a Varian model 475 digital integrator. The integrator was calibrated by injecting known quantities of each compound. Carbon dioxide was identified by the precipitation of barium carbonate from aqueous barium hydroxide and quantitatively analyzed by titration with oxalic acid. Water was quantitatively analyzed by g.l.c., using the thermal-conductivity detector. The charred residue left after 20 min at 600° was weighed in the original aluminum boats. The amount of levoglucosan that had evaporated and tar that was formed coated the pyrolysis tube and other parts of the instrument and could not be directly estimated.

Evaporation of 1,6-anhydro-β-D-glucopyranose. — The anhydro sugar (9.2 mg) was placed in a sublimation tube and heated in an oil bath at 220° for 4 min. The material was completely evaporated after this period and was recovered as a condensate (8.3 mg) which was silylated and analyzed by g.l.c. This showed only one peak corresponding to the anhydro sugar derivative.

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REFERENCES

1 F. Shafizadeh, *Advan. Carbohyd. Chem.*, 23 (1968) 419.
2 C. T. Greenwood, *Advan. Carbohyd. Chem.*, 22 (1967) 483.
3 S. Glassner and A. R. Pierce III, *Anal. Chem.*, 37 (1965) 525.
4 K. Heyns and M. Klier, *Carbohyd. Res.*, 6 (1968) 436.
5 M. L. Wolfrom, A. Thompson, and R. B. Ward, *J. Amer. Chem. Soc.*, 81 (1959) 4623.
6 J. da S. Carbalho, W. Prins, and C. Schuerch, *J. Amer. Chem. Soc.*, 81 (1959) 4054.
7 I. J. Goldstein and T. L. Hullar, *Advan. Carbohyd. Chem.*, 21 (1966) 431.
8 F. Shafizadeh and G. D. McGinnis, *Carbohyd. Res.*, 16 (1971) 273.
9 F. Shafizadeh, G. D. McGinis, R. A. Susott, and C. W. Philpot, *Carbohyd. Res.*, 15 (1970) 165.
10 F. Shafizadeh, G. D. McGinnis, C. W. Philpot, and R. A. Susott, *Carbohyd. Res.*, 13 (1970) 184.
11 R. L. Whistler and J. N. BeMiller, *Advan. Carbohyd. Chem.*, 13 (1958) 326.
12 Elisabeth Dryselius, B. Lindberg, and O. Theander, *Acta. Chem. Scand.*, 12 (1958) 340.
13 G. A. Byrne, D. Gardiner, and F. H. Holmes, *J. Appl. Chem.* (London), 16 (1966) 81.
14 J. B. Berkowitz-Mattuck and T. Noguchi, *J. Appl. Polymer Sci.*, 7 (1963) 709.
15 J. C. Arthur, Jr. and O. Hinojosa, *Textile Res. J.*, 36 (1966) 385.
16 D. Williams, J. E. Geusic, M. L. Wolfrom, and L. J. McCabe, *Proc. Natl. Acad. Sci. U. S.*, 44 (1958) 1128.
17 R. F. Schwenker, Jr. and L. R. Beck, Jr., *J. Polymer Sci.*, C [2] (1963) 331.
18 G. A. Byrne, *J. Chromatogr.*, 20 (1965) 528.