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Note

Pyrolytic production and decomposition of 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose

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Pyrolysis of cellulose results in transglycosylation and preponderant formation of levoglucosan[1,2] (1,6-anhydro-β-D-glucopyranose). This reaction is, however, accompanied by some dehydration and charring, which are enhanced in the presence of acidic catalysts and the related flame-retardants[2–5]. Several laboratories have reported the isolation of similar dehydration products, identified as a 1,5-anhydro-2,3-dideoxy-β-D-pent-2-enofuranose[6] (**1**), *cis*-4,5-epoxy-2-pentenal[7] (**2**), and levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose)[8] (**3**).

In our studies on the pyrolysis of phenyl β-D-glucopyranoside[5], levoglucosan, and cellulose and its chlorinated and phosphorylated derivatives[9,10], we have also encountered the new dehydration product **3**; this compound is formed in small proportions when the pure materials are pyrolyzed, and in substantial proportions when an acidic catalyst is added (see Table I). This Table shows an increasing trend in the respective effectiveness of zinc chloride as a Lewis acid, diammonium hydrogen phosphate acting as a moderately acidic reagent under pyrolytic conditions by losing ammonia[11,12], and diphenyl hydrogen phosphate as a strong Arrhenius acid[13].

The new compound exhibited the same infrared (i.r.), ultraviolet (u.v.), and mass spectra as reported for levoglucosenone[8], and the same i.r. and mass spectra as reported for *cis*-4,5-epoxy-2-pentenal[7] (**2**). It also gave the same retention time as that reported for **2** in gas–liquid chromatography (g.l.c.), and a single peak when the two samples were mixed. Compound **3** was characterized by a crystalline (2,4-dinitrophenyl)hydrazone (DNPH) derivative, found to be identical with the DNPH derivative prepared from **2** [on the basis of thin-layer chromatography (t.l.c.), melting point, and mixed melting point]. However, the elemental analysis of the DNPH derivative closely matched the results expected from the levoglucosenone formula and therefore, confirmed the 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (**3**) structure.

As shown in Fig. 1, the yield of levoglucosenone was drastically lessened at higher temperatures, indicating that it is readily decomposed under the pyrolytic conditions. In view of the significance of the dehydration and charring pathway for

TABLE I

YIELDS OF LEVOGLUCOSENONE (3) FROM THE PYROLYSIS OF CELLULOSE, PHENYL β-D-GLUCOPYRANOSIDE, AND LEVOGLUCOSAN AT 350°

Sample	*Yield (%)*[a]
Cellulose	1.8
+5% of zinc chloride	3.8
+5% of diammonium hydrogen phosphate	9.3
+5% of diphenyl hydrogen phosphate	12.3
Phenyl β-D-glucopyranoside	1.6
+5% of zinc chloride	3.9
+5% of diammonium hydrogen phosphate	6.5
+5% of diphenyl hydrogen phosphate	10.4
Levoglucosan	1.2
+5% of zinc chloride	1.2
+5% of diammonium hydrogen phosphate	4.5
+5% of diphenyl hydrogen phosphate	6.9

[a]Based on the content of sugar anhydride.

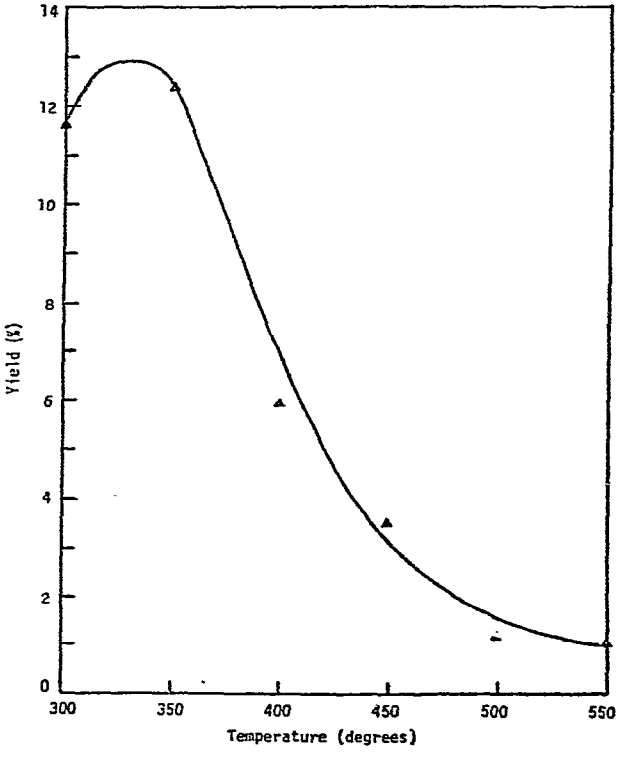


Fig. 1. The yield of levoglucosenone from the pyrolysis of cellulose treated with 5% of diphenyl hydrogen phosphate at different temperatures.

the flameproofing of cellulosic materials[1], the fate of this compound at higher temperatures was investigated by dynamic, thermal analysis and by isothermal pyrolysis.

The thermal analysis data (see Fig. 2) indicated that the pure compound is very volatile, and evaporates completely at 100–150°. However, when zinc chloride was added, a substantial part of the organic compound decomposed, leaving about 20% of a carbonaceous residue at 400°. Interestingly, diammonium hydrogen phosphate and diphenyl hydrogen phosphate had little or no effect. As zinc chloride is a strong dehydration catalyst, these data seem to indicate that the low yields obtained in the presence of this catalyst (see Table I) are due to the decomposition of levoglucosenone under the conditions under which it is formed. These data also verify the difference between the dehydration and charring reactions. As noted in a previous publication in this series[5], the charring reactions, in addition to dehydration, involve condensation, and decomposition of the condensation products, followed by homolytic elimination of the carbon substituents.

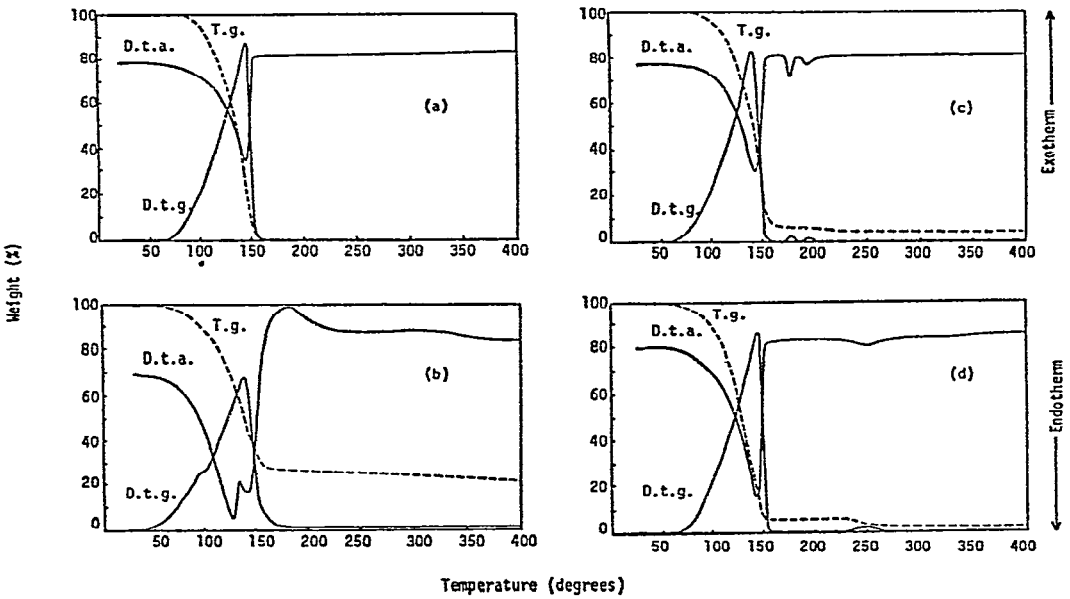


Fig. 2. Thermal analysis of levoglucosenone samples: (a) neat, (b) +5% of zinc chloride, (c) +5% of diammonium hydrogen phosphate, and (d) +5% of diphenyl hydrogen phosphate. [D.t.a., differential thermal analysis, d.t.g., derivative thermogravimetry, and t.g., thermogravimetry; d.t.a. on the right-hand scale, t.g. on the left-hand scale.]

The dynamic, thermal-analysis data were confirmed by the results obtained from isothermal pyrolysis at 550°, shown in Table II. In this process, about 76% of the original material remained unpyrolyzed in the tar and volatile fractions obtained from the untreated sample. In addition to the intact material, the volatile fraction

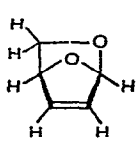
TABLE II

PYROLYSIS PRODUCTS OF LEVOGLUCOSENONE (3) AT 550°

Product	*Yield (%)*[a]			
	Neat	*+5% of $ZnCl_2$*	*+5% of $(NH_4)_2HPO_4$*	*+5% of Ph_2HPO_4*
Acetaldehyde	1.7	1.1	2.4	1.9
2-Furaldehyde	T[b]	5.1	T	T
5-Methyl-2-furaldehyde	1.8	1.5	1.7	2.1
5-Methylene-3-cyclopentene-1,2-dione	1.9	1.8	1.7	—[c]
Unpyrolyzed levoglucosenone in the volatile fraction	4.2	0.6	4.0	4.9
Carbon dioxide	0.9	3.1	1.2	0.6
Water	1.3	10.3	1.9	2.1
Char[d]	3.0	21.4	4.4	4.1
Tar[d]	76.3	67.0	72.2	76.4
Levoglucosenone content of the tar[e]	(94.0)	(68.5)	(91.2)	(96.3)
Total unpyrolyzed levoglucosenone	(75.9)	(46.5)	(69.8)	(78.5)

[a]Based on the weight of levoglucosenone. [b]T = trace amount. [c]Phenol peak coincided with this peak; therefore, the amount could not be determined. [d]Based on the total weight of the sample. [e]Based on the weight of tar.

contained small proportions of acetaldehyde, 5-methyl-2-furaldehyde, carbon dioxide, water, and an unknown compound tentatively identified as 5-methylene-3-cyclopentene-1,2-dione (**4**) on the basis of its i.r., u.v., and mass spectra. The addition of zinc chloride significantly increased the degree of decomposition, and the yields of 2-furaldehyde, carbon dioxide, water, and char, by enhancing further dehydration and charring reactions. Addition of diammonium hydrogen phosphate and diphenyl hydrogen phosphate, as in the dynamic, thermal-analysis process, did not materially alter the thermal reactions involved.



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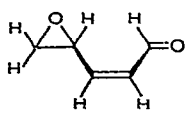

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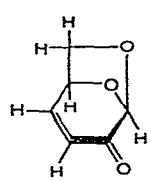

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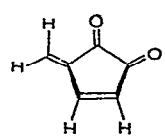

4

EXPERIMENTAL

Preparation of samples. — The treated samples were prepared by grinding the compound and additive together into a homogeneous mixture. All the samples were dried *in vacuo* below 50°, and stored under anhydrous conditions.

Levoglucosenone (**3**) was prepared by the pyrolysis of microcrystalline cellulose

as described by Halpern and co-workers[8]. The chemically treated samples of **3** were prepared by mixing a powdered additive with the compound.

Identification of levoglucosenone (**3**). — The isolated compound was identified on the basis of its i.r., u.v., and mass spectra, which were identical to those reported by Halpern and co-workers[8]. The DNPH derivatives were obtained by adding small samples of levoglucosenone to a saturated solution of (2,4-dinitrophenyl)hydrazine in M hydrochloric acid. The product crystallized from ethanol, had m.p. 214–215°, $[\alpha]_D^{26}$ −122° (chloroform), and R_F 0.29 (t.l.c. on silica gel developed with 19:1 benzene–tetrahydrofuran).

Anal. Calc. for $C_{12}H_{10}N_4O_6$ (DNPH derivative of levoglucosenone): C, 47.06; H, 3.30; N, 18.30; O, 31.34. Found: C, 46.97; H, 3.22; N, 18.20; O (by difference), 31.61. [Calc. for $C_{11}H_{10}N_4O_5$ (DNPH derivative of *cis*-4,5-epoxy-2-pentenal): C, 47.48; H, 3.63; N, 20.14; O, 28.75.]

Thermal analysis. — The d.t.a. (differential thermal analysis) data were obtained with a DuPont Model 990 Thermal Analyzer equipped with a cell for differential scanning calorimetry. All experiments were performed with 2-mg samples in 6-mm, aluminum pans, and an empty pan was used as the reference. The samples were heated at the rate of 15°.min^{-1} in a flow of nitrogen of 75 ml.min^{-1}.

A Cahn R-100 electrobalance was used for thermogravimetry (t.g.). A DuPont thermal analyzer was used to program a furnace surrounding the balance tube. The derivative (d.t.g.) of the t.g. signal was taken with a Cahn time–derivative computer (Mark II).

Pyrolysis. — Two types of pyrolysis unit were used in this study. In the first system, a sample (3–4 mg) was pyrolyzed in a preheated, modified Perkin–Elmer Pyrolysis Unit which was connected directly to the carrier-gas stream of an F and M Model 5750 temperature-programmed gas chromatograph with a column (3.66 m) of 10% of 20M Carbowax. A Varian Model 475 digital integrator was connected to the g.l.c. instrument for quantitative analysis of volatile compounds.

The second pyrolysis system was used to determine the amount of char, tar, and carbon dioxide. The sample (25–35 mg) was pyrolyzed in a Sargent Micro-combustion Apparatus under conditions similar to those used in the g.l.c. pyrolysis unit. Carbon dioxide was quantitatively determined by bubbling the effluent through aqueous barium hydroxide, and titrating the remaining barium hydroxide solution with oxalic acid. Char was defined as the residue left in the combustion boat after 5 min at 550°, and tar was defined as the material that condensed at room temperature on the pyrolysis tube downstream from the heater.

Identification of volatile products. — Acetaldehyde, 2-furaldehyde, and 5-methyl-2-furaldehyde were identified by comparing their g.l.c. retention-times, t.l.c. R_F values, melting points, and mixed melting points of their DNPH derivatives with those of authentic samples.

5-Methylene-3-cyclopentene-1,2-dione (**4**) was identified from its i.r., u.v., and mass spectra. The i.r. spectrum exhibited absorptions at the following frequencies: 3390 (broad), 1720 (broad and split), 1600 (split), 1240, 765, and 705 cm^{-1}. The u.v.

spectrum exhibited absorption of λ_{max}^{MeOH} 210 nm and two smaller absorption peaks of λ_{max}^{MeOH} 274 and 280 nm. The mass spectrum showed a parent peak at *m/e* 108 (relative intensity 7.7). Other fragments were *m/e* 107 (11.5), 94 (100.0), 66 (34.6), 65 (23.0), 40 (15.4), and 39 (26.9).

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