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YIELD OF 1,6-ANHYDRO-3,4-DIDEOXY-β-D-*glycero*-HEX-3-ENOPYRANOS-2-ULOSE (LEVOGLUCOSENONE) ON THE ACID-CATALYZED PYROLYSIS OF CELLULOSE AND 1,6-ANHYDRO-β-D-GLUCOPYRANOSE (LEVOGLUCOSAN)

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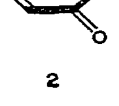
ABSTRACT

Although 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (**2**) is produced by the acid-catalyzed pyrolysis of both cellulose and 1,6-anhydro-β-D-glucopyranose (**1**), data presented here show that the principal mechanism of its formation in the pyrolysis of cellulose is not via **1**. Furthermore, the data provide evidence that **1** itself is not a primary product of cellulose pyrolysis, so that the principal mechanism of its formation must involve a precursor as yet unidentified.

INTRODUCTION

In 1970, Tsuchiya and Sumi[1] demonstrated that on pyrolysis of cellulose with acidic fire retardants a new unidentified compound replaced 1,6-anhydro-β-D-glucopyranose (levoglucosan, **1**) as the major constituent of a still significant tar fraction. In 1973, Halpern, Riffer, and Broido[2] identified the new tar constituent as 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (levoglucosenone, **2**), and demonstrated that it was produced by the acid-catalyzed pyrolysis of both cellulose and **1**. Thorough mixing of the acid catalyst and carbohydrate was shown to be unnecessary—it being sufficient to pass the pyrolysis vapors over catalyst-impregnated glass wool. Halpern *et al.* proposed a mechanism for the acid-catalyzed dehydration of **1** to **2**. The present work was undertaken to establish whether production of **2** in the acid-catalyzed pyrolysis of cellulose proceeds via **1**. In the process, the experiments also provided evidence that **1** itself is not a primary product of cellulose pyrolysis.



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EXPERIMENTAL

Pyrolysis methods. — The experiments were conducted by using a series of three concentric glass tubes (Fig. 1) mounted within a 3 x 32 cm horizontal glass tube sealed at the end to be mounted in a tube furnace. This outermost "pyrolysis tube" extended roughly half its length beyond the furnace and was connected to a vacuum line via a trap cooled with Dry Ice in 2-butoxyethanol. The 1 x 4 cm innermost tube was sealed at one end and contained the carbohydrate sample, held in with a wad of clean glass wool. This "sample tube" was inserted with open end facing the closed end of a 1.3 x 10 cm culture tube ("treatment tube"). It was held in place with clean glass wool, or, when appropriate, two wads of catalyst-impregnated glass wool sandwiched between two wads of clean glass wool. In turn, the treatment tube was inserted into a 1.6 x 33 cm "collection tube", open at both ends and extending the full length of the pyrolysis tube and just beyond the first ground-glass joint.

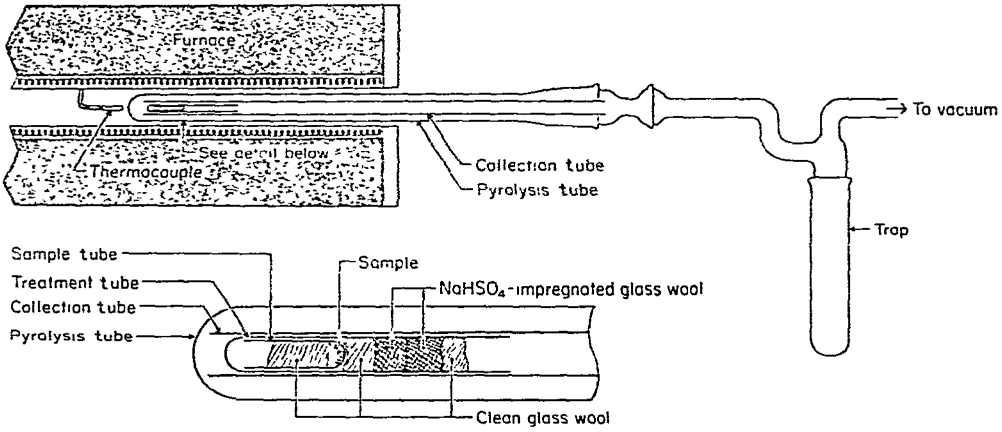

Fig. 1. Schematic of pyrolysis apparatus.

Three convenient starting pressures were available for these experiments. The house vacuum system, used for the experiments in which **2** was first identified[2], provided a pressure of 1.17×10^4 Pa (88 mmHg). The vacuum system made available for these experiments could reach 0.27 Pa (2 μmHg) by using the mechanical forepump alone, and 6.7×10^{-3} Pa (0.05 μmHg) with the oil-diffusion pump operating.

For the experiments at 10^4 Pa, the system was pumped down and dry nitrogen gas was added to give the desired pressure. With the small samples used (50–100 mg), the pressure of the closed system did not increase appreciably during the pyrolysis. On the other hand, the experiments at the lower pressures were conducted with continuous pumping, but with almost 10-fold increases in pressure measured in the vacuum system beyond the cold trap at peak evolution of the non-condensable pyrolysis gases.

For pyrolysis experiments in a vacuum, heat transfer is by radiation, and to maintain temperatures at about 300° this radiation must be largely in the infra-red region to which glass is opaque. Thus, the electric furnace must first heat the outer glass tube, which in turn transmits energy to its contents by radiation. With the apparatus available, the time-constant for such heating, after an appropriate time-lag for each layer of glass, was about 5 min (Fig. 2), as determined with fine chromel-alumel thermocouples in experiments conducted without samples.

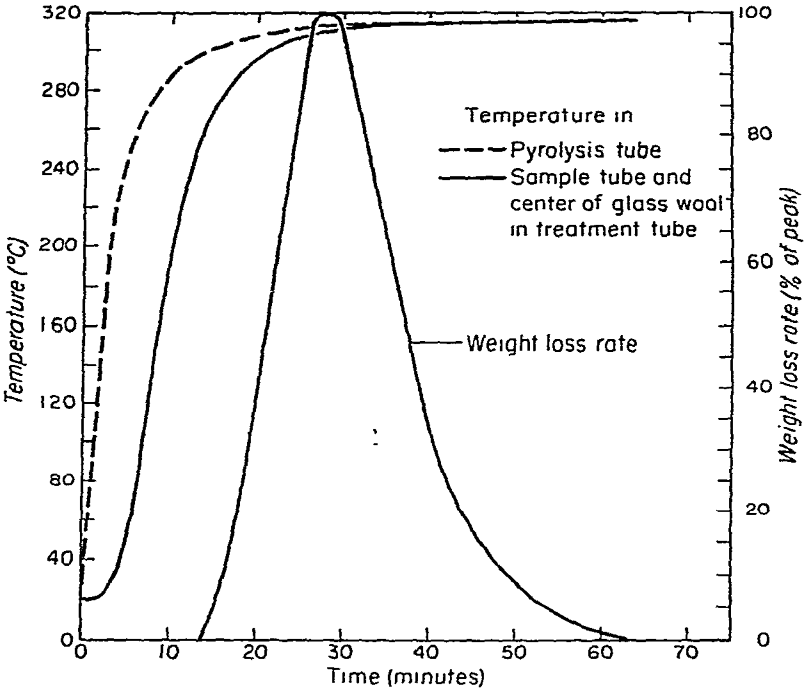

Fig. 2. Temperature increase inside pyrolysis tube inserted into furnace preheated to 315°. Also plotted is the curve for rate of weight loss (as percentage of maximum rate) for pyrolysis of cellulose following such a temperature history.

In an attempt to establish reasonably similar conditions for the two carbohydrates, experiments were conducted at three temperature settings: 295, 315, and 335°. Cellulose loses weight with a half-time of 4–5 min at 315°, and this half-time changes by a factor of about 6 in 20°. Thus, if the furnace is set at 315°, about 50% of the weight loss occurs at temperatures below 310° (Fig. 2). For settings above 315°, most of the cellulose reacts during an ill-defined warm-up period. Only at temperatures below 300° does the bulk of the reaction occur during the near-isothermal period. With a sufficiently high vacuum, pyrolysis for 2 h at 295° "distils" over more than 90% of the mass of a pure cellulose sample, and the "tar" yield contains about 50% of **1**.

Unlike cellulose, **1** begins to melt at about 180° and to volatilize at temperatures not much higher. In fact, at a sufficiently low pressure, some sublimation occurs even before melting. Thus, pyrolysis for 2 h with the furnace temperature at 295° distils over most of the **1**, but the distillation process may have been completed long before the temperature of the sample approaches furnace temperature. Visual observation during several non-quantitative experiments with the furnace partially open indicated that, at 10^4 Pa, melting occurred about 5 min before the first volatilization. Bubbling of the sample as a result of evaporation and degradation (the melt turned progressively darker brown) then continued for an additional 10 min.

At the lower pressures, **1** sublimed or distilled from the sample tube during ~2 min. The subsequent experiments demonstrated that the vapors did not pass through the catalyst at temperatures too low for significant reaction to take place. However, a limited number of experiments were performed in which (*a*) the heating of the sample was further slowed by inserting it in a small glass capsule inside the sample tube, and (*b*) the heating of the treated glass plug was speeded by using an electric heating-tape before inserting the pyrolysis tube into the furnace.

Times chosen (to ensure nearly complete pyrolysis of the cellulose) were 2 h at 295°, 1 h at 315° (40 min at 10^4 Pa), and 35 min at 335°. All times were measured from insertion of the pyrolysis tube into the preheated furnace. At the prescribed time, the furnace was removed and the tube was allowed to cool to room temperature before air was introduced.

Materials. — Each experiment on cellulose used 100 mg of powdered Cellex MX (Bio-Rad Laboratories, Richmond, Calif.) neat or mixed with an equal weight of sodium hydrogen sulfate. Pyrolysis of pure cellulose yielded about 50 mg of **1** in this apparatus, and to simplify direct comparison, parallel experiments were performed on 50-mg samples of **1** (prepared and purified by the procedure of Ward[3]), also neat or mixed with an equal weight of salt. For mixing with the carbohydrates, $NaHSO_4 \cdot H_2O$ was first dried for 2 h at 350°. A weighed quantity of the anhydrous salt was then mixed (mortar and pestle) with an equal weight of carbohydrate. For experiments in which the vapors were to be passed over salt-treated glass wool, the wads of glass wool were treated with an aqueous sodium hydrogen sulfate solution, dried slowly, and heated for 2 h at 350° before use.

Analytical methods. — Weight changes were determined for the collection tube alone, the treatment tube containing the sample tube, and the sample tube alone. A dichloromethane-soluble tar fraction and a pyridine-soluble tar fraction were also weighed. Two solvents were used because **2** decomposed on being kept in pyridine and **1** is relatively insoluble in dichloromethane. The amount of **2** present in the dichloromethane solution was determined by gas chromatography, using a Packard model 7831 instrument with a flame-ionization detector. At first, diphenylmethane and, later, phenol were used as internal standards. The combined tars, in 2 ml of pyridine, were (trimethylsilyl)ated by adding 0.2 ml of hexamethyldisilazane and 0.1 ml of chlorotrimethylsilane, and the amount of **1** present was determined with diphenylmethane or anthracene as the internal standard.

For these analyses, the carrier gas was helium. The 1.5 m × 2 mm glass column contained a 7:3 mixture of 10% SE-30 and 10% Carbowax 20M on 60–80 mesh Chromosorb W. The injector and detector temperatures were maintained at 235°. The experiments with diphenylmethane as the internal standard for both **1** and **2** involved a programmed temperature-regime from an initial column temperature of 141° to a final temperature of 220°. For most of the experiments, the columns were operated isothermally at a temperature of 123° with phenol as the internal standard for **1**, and at 213° with anthracene as the internal standard for **2**.

RESULTS

The reported yields of gross "tar" fraction and of **1** and **2** (Tables I–III) are each based on one to three experiments.

At the two lower pressures used, neat compound **1** began to sublime (as detected by condensation outside the furnace) 7–8 min after heating was started. Transfer from the sample tube was quantitative and analysis of the collected "tar" (Table I) indicated a 90% recovery of **1** with no detectable **2**. However, at 10^4 Pa, sublimation did not occur, and condensation outside the furnace was not observed until 12–15 min after the start. Because of increased residence-time in the heated zone, polymerization and further pyrolysis occurred while the sample was evaporating. Consequently, the tar fraction was decreased considerably. About half of the balance remained as char within the sample and treatment tubes, and about half was evolved as water and non-condensable gas.

TABLE I

YIELDS OF TAR, LEVOGLUCOSAN (**1**), AND LEVOGLUCOSENONE (**2**) FROM HEATING OF PURE CELLULOSE OR LEVOGLUCOSAN

Pressure (Pa)	*Temp. (°C)*	*Yield (mg) from 100 mg of cellulose*			*Yield (mg) from 50 mg of levoglucosan* (**1**)		
		Tar	**1**	**2**	*Tar*	**1**	**2**
6.7×10^{-3}	295	78	44	0.6	48	47	0
	335	70	48	1.0	44	42	0
0.27	315	80	45	0.6	48	45	0
	335	72	47	0.8	50	46	0
1.17×10^{4}	295	43	9	1.3	39	16	0
	315	45	13	0.7	30	16	0

When compound **1** was mixed with an equal weight of anhydrous sodium hydrogen sulfate and heated, almost total degradation of the carbohydrate resulted. The tar yields did not exceed 2–3 mg. Since g.l.c. analyses of these samples were intermingled with others involving yields 50 to 500 times higher, even the small values reported (Table II) may be the result of a small amount of contamination carried over from prior measurements.

TABLE II

YIELDS OF TAR, LEVOGLUCOSAN (1), AND LEVOGLUCOSENONE (2) FROM HEATING OF CELLULOSE OR LEVOGLUCOSAN MIXED WITH AN EQUAL WEIGHT OF ANHYDROUS $NaHSO_4$

Pressure (Pa)	*Temp. (°C)*	*Yield (mg) from 100 mg of cellulose*			*Yield (mg) from 50 mg of levoglucosan* (**1**)		
		Tar	**1**	**2**	*Tar*	**1**	**2**
6.7×10^{-3}	295	47	29	6.2	3	0.4	0
	315	47	18	5.7	2	0.1	0.1
0.27	295	50	26	6.9	3	0.3	0.1
	315	57	24	6.1			
1.17×10^{4}	295	10	0	0.5			
	315	8	0.2	1.3	2	0	0

When the vapors obtained on heating pure **1** were passed through similarly heated glass wool impregnated with sodium hydrogen sulfate, condensation outside the furnace was not observed until 9–12 min—well after the material in the sample tube had melted and begun to bubble vigorously. The experiments in which the glass-plug section was preheated before the furnace was moved into place gave erratic results and are not included in Table III. In general, yields of **1** were appreciably lower than those without preheating, but occasionally a very high yield was inexplicably obtained.

TABLE III

YIELDS OF TAR, LEVOGLUCOSAN (1), AND LEVOGLUCOSENONE (2) FROM PASSING PYROLYZATE VAPORS THROUGH GLASS WOOL IMPREGNATED WITH ANHYDROUS $NaHSO_4$

Pressure (Pa)	*Temp. (°C)*	*Yield (mg) from 100 mg of cellulose*			*Yield (mg) from 50 mg of levoglucosan* (**1**)		
		Tar	**1**	**2**	*Tar*	**1**	**2**
6.7×10^{-3}	295	56	23	2.6	30	13	1.7
	315	64	35	1.4	32	12	1.1
	335	65	37	1.9	28	15	1.2
0.27	295	68	18	1.7	31	6.7	0.7
	315	61	27	1.0	40	4.7	0.3
	335	66	37	1.3	22	5.9	1.4
1.17×10^{4}	295	20	0.3	4.8	11	0	2.0
	315	21	0	6.2	14	0.1	2.3

Depending on temperature, condensation of pyrolyzates from cellulose at the two lower pressures was first observed after 12–18 min. Weight loss from the sample tube averaged 92.1 ±1.5%. At 10^4 Pa, first condensation was observed 1–2 min earlier than for the corresponding low-pressure experiments. Weight loss from the sample tube averaged 72.0 ±2.6%.

Post-experiment observation of the reaction tubes in these experiments clearly indicated a difference between the two carbohydrates. In general, weight loss from the reaction tube–sample tube system was about the same as weight loss from the sample tube alone. In a number of experiments involving **1** and sodium hydrogen sulfate, however, weight loss from the sample tube alone was significantly greater than that from the two-tube system (in two experiments the difference was more than 10 mg) as a result of char formation on the glass wool. In the experiments with cellulose, the first, untreated glass-wool plug usually was darkened with a small amount of solid pyrolyzate (smoke); in contrast, the salt-treated glass-wool section generally appeared quite white. On the other hand, when **1** was heated, the untreated glass wool generally remained clean. The greatest darkening appeared at the leading edge of the salt-treated plug—with the discoloration tapering off with depth into the treated section. Clearly, the darkening in the case of cellulose was the result of filtering of a previously formed smoke or char, whereas in the case of **1** it resulted from reactions catalyzed by the salt.

CONCLUSIONS

Heating the mixture of salt and compound **1** resulted in almost total degradation of **1**, whereas the cellulose–salt experiments at lower pressures did yield large amount of **1**. These two facts suggest quite strongly that formation of **1** from pyrolysis of cellulose does not occur until the pyrolyzate has left the carbohydrate–salt matrix (that is to say, **1** must have a volatile precursor in the pyrolysis scheme). Furthermore, the relatively low yields of **1** found when pure **1** is heated even at low pressure and the vapors are passed through a plug impregnated with sodium hydrogen sulfate confirm the high reactivity of gaseous **1** in such a matrix. The presence of other volatile pyrolytic products from cellulose, including water and organic acids, can only serve to decrease further the probability that **1** could pass through the matrix without reacting. Thus, the relatively high yields of **1** when the vapors formed by pyrolysis of cellulose at low pressure are passed through the salt plug leads to the apparently inescapable conclusion that formation of **1** on pyrolysis of cellulose does not occur until a volatile precursor has passed beyond the point of contact with the hot salt catalyst, and thus no more than a minor fraction of the yield can be produced as a primary product of cellulose pyrolysis.

Appreciable yields of **2** were obtained in the pyrolysis of neat cellulose, but no **2** was found on heating pure **1**, even though considerable pyrolysis of **1** occurred at 10^4 Pa. Even heating **1** mixed with anhydrous sodium hydrogen sulfate produced essentially no **2**. On the other hand, at lower pressures the mixing of sodium hydrogen sulfate with cellulose increased the yields of **2** by almost a factor of ten.

The most obvious explanation for the decreased yields of both **1** and **2** in the cellulose–salt experiments at higher pressure is that, with the resultant increase in residence time, further degradation of these products occurs. In addition, the almost total disappearance of **1** implies that, in contact with sodium hydrogen sulfate, compound **1** is degraded much more rapidly than is the precursor in its formation from cellulose, and the longer residence time permits the intermediate compound to be converted into **1** before passing beyond the solid matrix.

The decreased yields of the tar components at higher pressure in the mixed cellulose–salt experiments also raise a question about the experiments in which the carbohydrates are heated in neat form and the vapors are passed over the salt-treated glass wool. Although measured pressures did not increase by more than an order of magnitude during the low-pressure pyrolyses, those measurements do not preclude the possibility that **1** from pyrolysis of cellulose passed through the treated glass wool at low pressure as it was formed, but that, on starting with **1**, it was distilled over in one rapid high-pressure pulse. However, this possibility is precluded by the visual observation that sublimation–distillation of **1** takes place over a period of minutes, not fractions of a second, and probably during times similar in magnitude to those for the major portion of the cellulose pyrolysis at 335°. Furthermore, the fact that only without an intervening salt plug is condensation outside the furnace observed before melting of the sample means that, even at the relatively low rates of vapor evolution of **1** during sublimation, no significant amounts pass the catalyst without reacting.

The yields of **2** on passing vapors of **1** over sodium hydrogen sulfate confirm the existence of a mechanism for production of **2** via **1**. However, the much higher yields relative to loss of **1** in the parallel experiments with cellulose, together with the results of the neat and mixed carbohydrate–salt experiments, seems to provide overwhelming evidence that another mechanism (perhaps via the intermediate in formation of **1**) predominates. The very high yields of **2** in the similar experiments at higher pressure with cellulose, coupled with the disappearance of **1** in those experiments, is attributable to the combined yield from both mechanisms.

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