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Microwave pyrolysis of cellulosic materials for the production of anhydrosugars

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Abstract Large-scale microwave rapid pyrolysis of cellulosic materials has been investigated. Levoglucosan (1,6-anhydro- β -D-glucopyranose) was obtained from a larch log as the main anhydrosugar in 2.6% yield on the basis of dry wood weight. This yield would be much higher than that obtainable by conventional pyrolysis in the large-scale reaction. Levoglucosenone (1,6-anhydro-3,4-dideoxy- β -D-glycero-hex-3-enopyranose-2-ulose) was found to be produced in one-quarter the amount of levoglucosan. Other anhydrosugars, such as mannosan (1,6-anhydro- β -D-mannopyranose), galactosan (1,6-anhydro- β -D-galactopyranose), and xylosan (1,4-anhydro- α -D-xylopyranose), were also confirmed to be produced as minor components depending on the proportion of the monosaccharide content in the larch. When microwave pyrolysis of used papers and filter papers was performed, the yields of levoglucosan were about 6% and 12%, respectively, suggesting that a higher content of cellulose gives a larger amount of levoglucosan.

Key words Microwave pyrolysis · Cellulosic material · Anhydrosugars · Levoglucosan · Mannosan

Introduction

Levoglucosan (1,6-anhydro- β -D-glucopyranose) is an important starting material not only for preparing natural

products with chiral centers but also for the synthesis of stereoregular polysaccharides that have specific biological activities, such as anti-human immunodeficiency virus and blood anticoagulant activities.^{1–7} So far, levoglucosan has been prepared by conventional pyrolysis of cellulose or starch under reduced pressure,^{8–10} and the intramolecular dehydration of D-glucose between the C₁ and C₆ hydroxyl groups.^{11,12} Other anhydrosugars, such as mannosan (1,6-anhydro- β -D-mannopyranose), galactosan (1,6-anhydro- β -D-galactopyranose), and xylosan (1,4-anhydro- α -D-xylopyranose), were prepared in a similar manner.¹³ However, these methods are troublesome and require expensive pretreatment of the samples (e.g., acid washing or pulverization), and the scale of the reaction is too small to obtain a large amount of levoglucosan.

On the other hand, microwave heating has been recognized as a powerful technology for organic synthesis and the processing of polymers.^{14,15} Allan et al.¹⁶ and Straathof et al.¹⁷ reported the formation of levoglucosan by microwave heating a small amount of cellulose samples. These reports disclosed a significant difference between conventional and microwave heating systems. For conventional gas or electric heating of wood with poor thermal conductivity, the pyrolysis involving heat transfer proceeds from outside to inside. As a result, volatile matters generated inside would be further decomposed by passing through an outside zone at higher temperatures. For microwave irradiation, in contrast, heat flows from inside to outside. In this situation, a useful and unstable product such as levoglucosan can move toward the outside without serious degradation compared to that seen with the conventional system.

Recently, we have reported the preliminary microwave pyrolysis of wood using a modified household microwave oven.^{18–20} In this way, a relatively large log can be pyrolyzed within a short irradiation time and without costly pretreatment to produce levoglucosan and charred residue with a large specific surface area.

In this paper we report a further study on larger-scale microwave rapid pyrolysis of cellulosic materials for the production of anhydrosugars. In addition to levoglucosan, production of other anhydrosugars by pyrolysis was investi-

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gated to confirm them, as suggested previously.²¹ Used papers, filter papers, and larch log were examined as to whether the cellulose content of samples has an influence on levoglucosan yields.

Experimental

General method

Cellulosic materials used in the present study included three samples: larch (*Lalix leptolepis* Gordon), used papers, and filter papers. Cylindrical larch logs (ca. 190 g of 80 mm diameter and 80 mm height; ca. 350 g of 100 mm diameter and 100 mm height) were supplied from Shimokawa Furusato Kogyo Kyodo Kumiai. Used paper was obtained from a local telephone directory (ca. 200 g of 70 mm width, 90 mm depth, and 55 mm height). Filter paper no. 5A (ca. 200 g of 90 mm diameter, 240 sheets) was obtained from Advantec. The moisture content of the samples was measured by a Sanko wood moisture meter (model TH-2C). Column chromatography and thin-layer chromatography were performed on silica gel (Merck Art. 9025 and 5715, respectively). The melting point was determined using a 500-D Yanagimoto micromelting point apparatus and was uncorrected. Levoglucosan, mannosan, and galactosan were purchased from Sigma-Aldrich Chemical Co. Xylosan was prepared by pyrolysis of D-xylose.²² Levoglucosenone and other reagents were supplied from Tokyo Kasei Organic Chemicals and Wako, respectively.

Microwave pyrolysis

Figure 1 represents the microwave heating apparatus. A Toshiba model TMG-132F variable 0.1–1.5 kW power generator at 2450 MHz was used to supply the microwave energy. The microwave oven was made of stainless steel with 370 mm i.d. and 460 mm height. The lower part of the oven was in the form of a funnel to suppress further thermal decomposition and facilitate recovery of any unstable pyrolysates, such as anhydrosugars. A sample cage made of quartz with a diameter of 8 mm was 120 mm wide, 120 mm

long, and 150 mm high; it was hooked over a motor in the oven. A cylindrical larch block was placed on the bottom of the sample cage in the microwave apparatus. Microwave pyrolysis was performed under a nitrogen atmosphere of 710 mmHg, as shown in Table 1. Used papers and filter papers were pyrolyzed at 160 V, as was the larch block. The product recovery was performed according to a previously reported procedure.²⁰

Product analysis

Gas chromatographic (GC) analysis was carried out on a Shimadzu GC-17A instrument equipped with an FID detector (a glass-capillary column, Shimadzu, CBP-10) (0.32 mm × 25 m × 0.5 μm; injector temperature 200°C; detector temperature 200°C; carrier gas He; flow rate 1.6 ml/min;

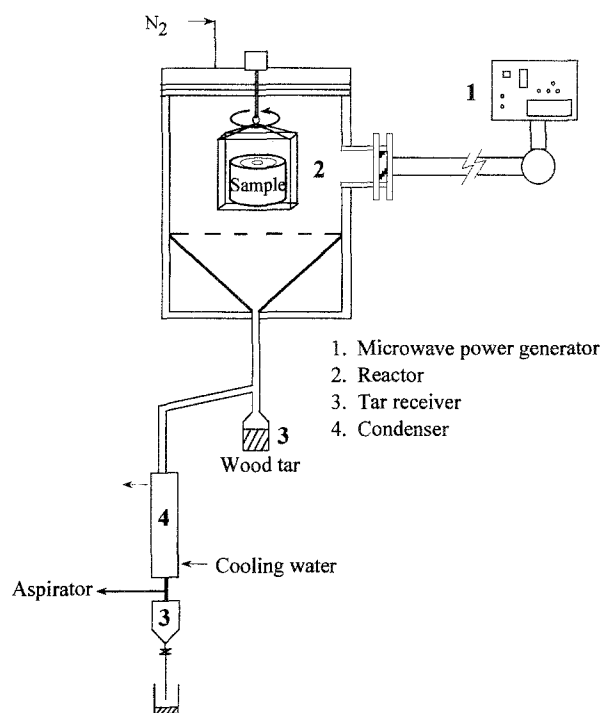


Fig. 1. Microwave heating apparatus

Table 1. Microwave pyrolysis of larch log

Sample no.	Larch log					Yield (wt%)		
	Diameter (mm ϕ)	Weight (g)	Water content (wt%)	Irradiation time (min)	Voltage (V)	Residue	Tar	LG ^a
1	80	186	11.4	3	140	90.2	–	–
2	80	188	10.8	6	140	49.4	10.5	0.7
3	80	189	11.8	9	140	32.8	12.6	1.1
4	80	187	11.7	12	140	22.1	24.0	1.4
5	80	190	11.6	15	140	20.9	22.5	1.9
6	80	191	11.9	18	140	20.1	18.1	1.1
7	100	348	10.9	11	150	20.6	25.9	2.6
8	100	349	10.9	14	150	21.5	16.7	1.2

Pressure in the reactor was 710 mmHg

^a Levoglucosan (based on the dry weight of larch log)

split ratio 1:40). The temperature of the column oven was programmed at 7.5°/min from 110°C to 260°C, and the final temperature was then maintained for 10 min. The content of the products in the tar obtained was determined as trimethylsilyl derivatives.²³ GC-mass spectrometry (GC-MS) spectra were obtained using a Shimadzu QP-2000 GC-mass spectrometer at 70 eV under electron impact conditions. The GC column and the temperature protocol were the same as described above.

Isolation of levoglucosan as triacetate (2,3,4-tri-*O*-acetyl-1,6-anhydro- β -D-glucopyranose)

To a magnetically stirred mixture of the tar obtained (78 g) (Table 1, no. 7) in ethyl acetate (300 ml) at 0°C were added acetic anhydride (120 ml, 1.27 mol), pyridine (97 ml, 1.34 mol), and a catalytic amount of (*N,N*-dimethylamino)pyridine (0.4 g, 3.3 mmol). The mixture was stirred overnight until no levoglucosan was detected by thin-layer chromatography. The excessive acetic anhydride was quenched with ethanol (30 ml, 0.52 mol) at 0°C, and the mixture was diluted with ethyl acetate (300 ml) and made alkaline with saturated sodium carbonate solution. The separated organic layer was washed with saturated brine, acidified with 6N hydrochloric acid, washed with saturated brine, dried with anhydrous sodium sulfate, and concentrated in vacuo. The crude acetylated mixture (92 g) was purified twice by silica gel column chromatography (600 g, 2:1 hexane/ethyl acetate) to afford crude triacetyl levoglucosan (12.8 g) as a yellow syrup. The syrup was recrystallized from methyl *tert*-butyl ether to yield the pure triacetate (8.8 g) as colorless crystals (mp 106°–107°C; lit.²⁴ mp 108°–109°C) and the mother liquor (3.9 g) as a yellow syrup.

Results and discussion

A GC analysis of the tar (Table 1, no. 7) indicated that levoglucosan appeared at a retention time of 13.5 min as a major product. The following compounds were also identified by GC analysis with the retention times (relative area ratios to levoglucosan are in parentheses): 2.1 min (0.25) for furfural, 3.4 min (0.25) for phenol, 4.2 min (0.11) for *o*-cresol, 5.0 min (0.14) for veratorol, 5.7 min (0.30) for guaiacol, 6.1 min (0.24) for levoglucosenone, 8.8 min (0.04) for xylofan, 9.6 min (0.16) for eugenol, 12.6 min (0.12) for galactosan, 13.2 min (0.27) for mannosan, and 13.5 min (1.0) for levoglucosan. The retention times of the detected compounds were identical with those of the authentic samples. GC analysis of the tar also showed that alcohols and aldehydes with low boiling points (e.g., furfural, phenol, *o*-cresol, veratorol, guaiacol, eugenol) originated from the lignin in the wood and appeared within 10 min. Peaks due to mannosan and galactosan were found to appear at around 13 min and were close to those of levoglucosan, as suggested previously.²¹ In addition, xylofan appeared as a minor component at around 9 min. Furthermore, it should be

noted that levoglucosenone (1,6-anhydro-3,4-dideoxy- β -D-glycero-hex-3-enopyranos-2-ulose), which dehydrated two molecules of water from levoglucosan, appeared at 6.1 min in one-quarter the amount of levoglucosan. It is a highly useful chiral starting material for preparing natural products as well as levoglucosan.¹ The retention times of these anhydrosugars were identical with those of the trimethylsilylated authentic samples. Based on the intensity of levoglucosan (1.0), the relative production of anhydrosugars in the tar was calculated to be 0.24 for levoglucosenone, 0.04 for xylofan, 0.27 for mannosan, and 0.12 for galactosan. Taking into account the relative proportion of the contents of the monosaccharide units in larch,²⁵ the anhydrosugars were produced by microwave pyrolysis depending on the amount of monosaccharides in the wood. In softwood, because xylose is a minor component and the content of xylose is lower than that in hardwood, xylofan was produced as a minor product in the tar. On the other hand, mannosan was found in the tar as a major product, because mannose has the second highest abundance (ca. 20%) in softwood.

The GC-MS analysis of the trimethylsilylated tar (no. 7) provided additional support for the production of the four anhydrosugars with the following retention times and electron ionization (EI)-MS *m/z* (rel. int.): for xylofan: 8.8 min, *m/z* (rel. int.) 217 (29.2), 215 (15.3), 147 (16.1), 75 (21.2), 73 (100); for galactosan: 12.6 min, *m/z* (rel. int.) 217 (81.5), 204 (15.8), 147 (10.7), 75 (13.7), 73 (100); for mannosan: 13.2 min, *m/z* (rel. int.) 217 (31.2), 204 (30.0), 147 (11.8), 75 (12.9), 73 (100); and for levoglucosan: 13.5 min, *m/z* (rel. int.) 217 (32.8), 204 (35.3), 147 (12.8), 75 (13.3), 73 (100). These fragmentations were identical with those of authentic xylofan, galactosan, mannosan, and levoglucosan, respectively. Thus, these anhydrosugars were found to be unambiguously confirmed in the wood tar by microwave pyrolysis on the basis of GC and GC-MS analysis. Tars obtained from larch log under other conditions, used paper, and filter paper were analyzed by GC in the same way, and the yields of levoglucosan are shown in Table 1 and Figs. 2 and 3, respectively.

Previously it was reported that levoglucosan, the major product in wood tar, could be isolated through a combination of several solvent extractions and gel permeation chromatography.²¹ The method is inefficient and troublesome, however, and only 5% of the levoglucosan in the wood tar can be obtained. On the other hand, it was found that most of the levoglucosan is easily isolated as the triacetate by acetylation and subsequent silica gel column chromatography.

To clarify the relation between microwave irradiation time and the yield of levoglucosan, the time was examined by fixing the voltage to the magnetron as shown in Table 1. It was found that the pyrolysis finished within 15 min at 140 V. The larch log was almost completely carbonized after irradiation for more than 12 min. When the larch log with a weight of about 190 g (80 mm diameter) was used (Table 1, samples 1–6), the yield of levoglucosan increased with an increase in the irradiation time up to 15 min. In sample 1, a 3-min irradiation exposure gave no tar, and water in the log was merely evaporated. However, it was found that the

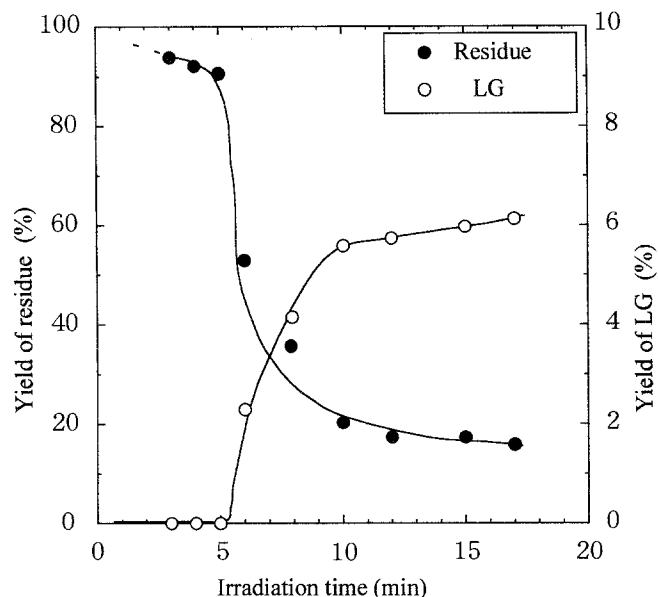


Fig. 2. Microwave pyrolysis of used paper. Sample: ca. 200 g (70 mm width \times 90 mm depth \times 55 mm height). Microwave conditions: 2450 MHz, 160 V, 13.2 A, 710 mmHg. LG, levoglucosan

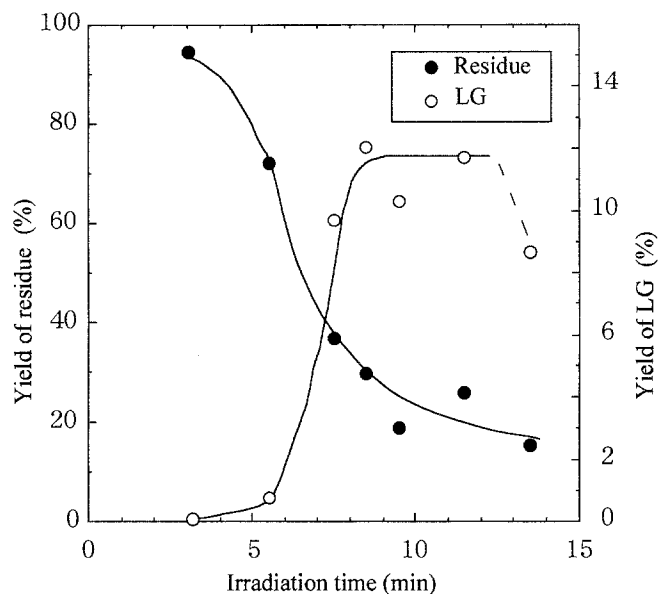


Fig. 3. Microwave pyrolysis of filter paper. Sample: ca. 200 g (90 mm diameter, 240 sheets). Microwave conditions: 2450 MHz, 160 V, 13.2 A, 710 mmHg

pyrolysis was rapid after 3 min of irradiation. In sample 5, the content and yield of levoglucosan were 7.4% in the tar and 1.9% on the basis of the log weight, respectively, after a 15-min irradiation period. In addition, it was revealed that the content and yield of levoglucosan increased with increasing weight of the larch log; that is, larch log weighing about 350 g (100 mm diameter) gave levoglucosan in 2.6% yield after a 11-min irradiation period at 150 V (sample 7). A further increase in the irradiation time did not improve the yield of levoglucosan, probably owing to further ther-

mal decomposition of the residual levoglucosan in the oven (nos. 6 and 8). Although the present microwave oven was designed to prevent further thermal decomposition of the anhydrosugars, the maximum yield of levoglucosan (2.6% from sample 7) was similar to that of the preliminary pyrolysis of the larch log (ca. 75 g of 60 mm diameter) using a modified household microwave oven.²⁰ A larch log about five times heavier than the first one was found to be similarly pyrolyzed by microwave heating without any costly pretreatment. This is a great advantage from a practical point of view because microwave heating does not require the expensive particle size reduction steps as previously suggested.^{16,20}

As for other cellulosic materials with a higher cellulose content, the microwave pyrolysis of used papers and filter papers proceeded smoothly and was found to produce levoglucosan in relatively good yields. When the microwave pyrolysis of used paper from a telephone directory and filter paper was carried out for 12 min, levoglucosan was obtained in 5.9% and 11.7% yields, respectively. Figure 2 shows the relation between the microwave irradiation time, the yield of levoglucosan, and the ratio of carbonized residue for microwave rapid pyrolysis of used paper. When the used paper was irradiated, pyrolysis occurred after 6 min of irradiation. As the irradiation time increased to 10 min, the yield of levoglucosan increased to about 6%. On the other hand, the weight of the residue left in the microwave oven decreased with an increase in irradiation time, and the residue was almost carbonized after 10 min of irradiation. The relative ratio of mannosan/levoglucosan in the tar obtained by 10 min of irradiation was estimated to be 0.11; trace amounts of galactosan and xylosan were detected.

In the case of filter paper, as shown in Fig. 3, the levoglucosan yield significantly increased to about 12% after 12 min of irradiation. The levoglucosan yield was greatly enhanced compared to the 2.5% yield in the preliminary pyrolysis study; the larch log samples had no effect on the yield.²⁰ After 12 min the levoglucosan yield decreased, probably owing to further thermal decomposition of the levoglucosan left in the microwave heating apparatus as mentioned before. In contrast to levoglucosan, other anhydrosugars were detected merely as small peaks, and thus the result provides support for filter paper to consist of nearly pure cellulose. The carbonized residue reached about 20 wt% of the initial weight of the filter paper after 13.5 min, suggesting that further irradiation leads to greater weight loss in the residue. These microwave pyrolysis results for the used papers and filter papers suggest that the yield of levoglucosan increases with an increase in the cellulose content.

Conclusions

Large-scale microwave rapid pyrolysis of cellulosic materials were investigated for the production of anhydrosugars. Levoglucosan was found to be a major product in the tars and was easily isolated as the corresponding triacetate.

Xylosan, galactosan, and mannosan were found for the first time to be produced in wood tar as minor components. Microwave pyrolysis, which proceeds within a short irradiation time using the log itself without costly pulverization steps, is a facile method and offers a great advantage over conventional pyrolysis by conduction heating. The present study has shown that microwave rapid pyrolysis of cellulosic materials can lead to the production of larger amounts of anhydrosugars. In addition, cellulosic materials with a high cellulose content, such as used paper and filter paper, can provide much higher yields of levoglucosan.

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