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Note

Thermal stabilization of levoglucosan in aromatic substances

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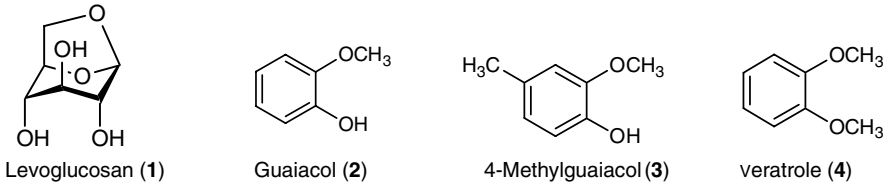
Abstract—Thermal degradation of levoglucosan (1,6-anhydro-β-D-glucopyranose) was shown to be substantially suppressed in the presence of some aromatic compounds under the conditions of N_2/240–340 °C/15 min. This stabilization effect is also discussed with CH–π interaction between levoglucosan and π-electrons in the benzene ring.

Keywords: Levoglucosan; Anhydrosugar; Thermal; Pyrolysis; Aromatic; CH–π interaction

Levoglucosan (1,6-anhydro-β-D-glucopyranose) (**1**) is an important primary pyrolysis product of various glucose-based carbohydrates such as cellulose and starch, and is known to be degraded further through various secondary pyrolysis reactions including thermal ring-opening polymerization.[1–5] In our previous papers, this polymerization reaction was proposed as a key reaction that determines the product composition of cellulose pyrolysis [i.e., low-molecular-weight (MW) products vs carbonized product].[6,7] We also found that thermal polymerization of levoglucosan was inhibited substantially during co-pyrolysis of cellulose with a lignin sample.[28] This paper describes the effects of various aromatic compounds, including model compounds **2**–**4** (Fig. 1) of lignin pyrolysate on thermal stabilization of levoglucosan. Furthermore, the stabilization mechanism is also discussed considering CH–π interactions.

Pure levoglucosan was converted into the products observed in the higher MW region in the GPC chromatogram (Fig. 2), and levoglucosan recovery was only 3.6% of the initial amount. Pictet[1] reported that levoglucosan polymerizes into dextran by heating at 240 °C for 15–30 min. Thus these high-MW products are considered to be the polymerized products through ring-opening of the bicyclic structure.

Addition of veratrole (**4**) to this system substantially reduced the polymerized product formation as shown in Figure 2. High-MW products decreased with an increase in the amount of **4** and almost completely disappeared at 2.0 mol equiv. Figure 3 summarizes the levoglucosan recovery against the amount of guaiacol (**2**), 4-methylguaiacol (**3**), or veratrole (**4**). Levoglucosan recovery increased with increasing amounts of aromatic compounds and became almost quantitative at



Levoglucosan (**1**) Guaiacol (**2**) 4-Methylguaiacol (**3**) veratrole (**4**)

Figure 1. Chemical structures of levoglucosan (**1**), guaiacol (**2**), 4-methylguaiacol (**3**), and veratrole (**4**).

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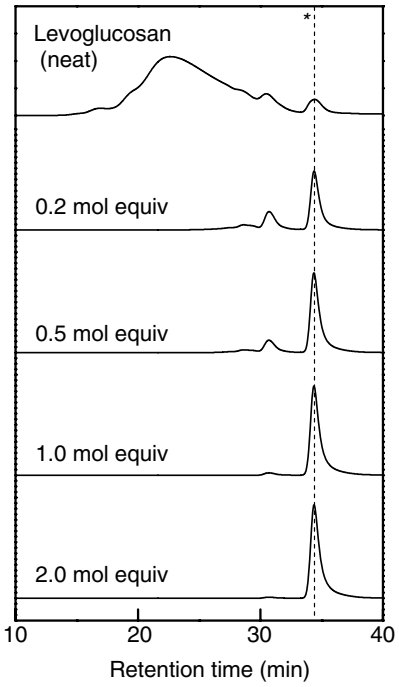


Figure 2. GPC chromatograms after heat treatment of levoglucosan–veratrole (**4**) under the conditions of N_2/240 °C/15 min: (*) retention time of levoglucosan; detector, RI.

1.0–2.0 mol equiv regardless of the chemical structures of aromatic compounds **2**–**4**. These results indicate that neither a phenolic OH nor a benzyl group has direct actions with levoglucosan related to the thermal stabilization. As shown in Figure 4, levoglucosan was recovered almost quantitatively up to 340 °C under the experimental conditions of levoglucosan (10 mg)/veratrole (100 μL)/N_2/15 min. It is also noted that these levoglucosan–aromatic compound mixtures became homogeneous during heat treatment. Interestingly, no other thermal decomposition reactions, including the

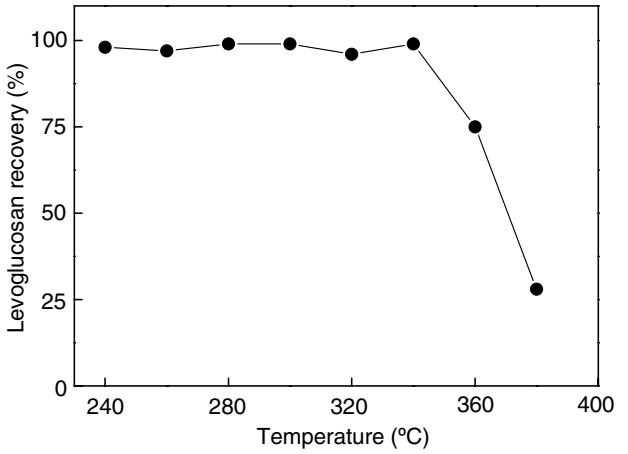


Figure 4. Effects of temperature on levoglucosan recovery in veratrole (**4**) after heat treatment in N_2 for 15 min.

formation of furfurals and dark-colored substances, were observed under these stabilizing conditions, even at a high temperature of 340 °C. These results suggest an interesting hypothesis that most of the thermal decomposition reactions are closely related to the ring-opening reaction of levoglucosan.

Dilution by aromatic compound, which reduces the accessibility of levoglucosan, is considered to be a reason for this stabilization. However, Kawamoto et al.[6] reported that levoglucosan solution in sulfolane (tetramethylene sulfone) was degraded into other low-MW products such as levoglucosenone and furfurals at 200–330 °C. From these results, some factors other than a diluting effect are indicated as a reason for this stabilization.

In the ^{1}H NMR analysis of a levoglucosan–guaiacol mixture in D_2O, the signals of H-4, H-5, and H-6 of levoglucosan were shifted toward higher magnetic fields with addition of an increasing amount of guaiacol (Fig. 5)

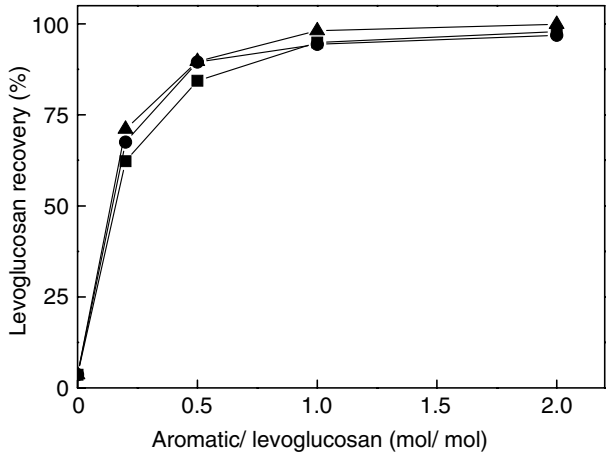


Figure 3. Levoglucosan recovery in aromatic compounds **2**–**4** after heat treatment under the conditions of N_2/240 °C/15 min: (●) guaiacol (**2**), (▲) 4-methylguaiacol (**3**), (■) veratrole (**4**).

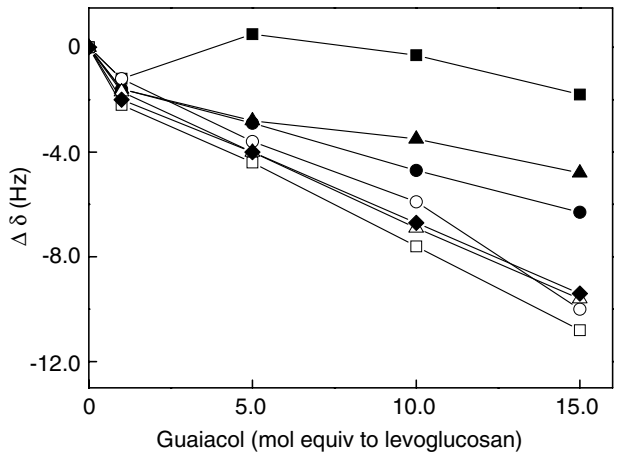


Figure 5. Effects of guaiacol (**2**) addition on the chemical shift of levoglucosan:protons observed in ^{1}H NMR analysis in D_2O: (●) H-1, (▲) H-2, (■) H-3, (○) H-4, (△) H-5, (□) H-6a, (♦) H-6b.

(assignment of each signal was conducted according to the report of Heyns and Weyer[8]). Similar shifts were also observed for H-1 and H-2 of levoglucosan, although the extent of the shifts is smaller than those of H-4, H-5, and H-6. On the other hand, the effect of guaiacol addition on the chemical shift of H-3 was comparatively very small. The signals assigned to H-3 and H-4, which were overlapped in the spectrum of pure levoglucosan, were separated in the spectra of the levoglucosan–guaiacol mixture due to higher magnetic field shifting of one signal. These signals were assigned with the ^{1}H–^{1}H COSY spectrum (Fig. 6).

Interaction between the C–H and π electron system (CH–π interaction)[9–27] is known to play important roles in conformation of some aromatic compounds,[11–14] the tertiary structure of protein[15,16] and molecular recognition.[10,17–23] As for sugar–aromatic interaction, Fernández-Alonso et al.[24] reported the association of the α face of methyl β-D-galactopyranoside with benzene or phenol through CH–π interaction from the ^{1}H NMR higher magnetic field shift observed for H-1, H-3, H-4, and H-5 of methyl β-D-galactopyranoside. Generally, C–*H* involved in the CH–π interaction is known to be observed in higher magnetic field in ^{1}H NMR analysis,[20–26] and the extent is positively related to the strength of the CH–π interaction.[25,26] Therefore, the results of ^{1}H NMR analysis in Figure 5 indicate the CH–π interaction of aromatic π electron with the H-4, H-5, H-6 face and the H-1, H-2 face of levoglucosan as illustrated in Figure 7. Stronger interaction of the H-4, H-5, H-6 face than the H-1, H-2 face is also indicated from the extent of the shifting. Although the data in Figure 5 are obtained in D_2O, similar complexation between levoglucosan and aromatic compounds is also considered in the neat system without D_2O.

Restricted thermal motion of levoglucosan in the complex is considered to be a reason for the stabilization effect, since thermal motion is a driving force in the thermal decomposition of levoglucosan. The ring-opening polymerization of levoglucosan into polysaccharides especially requires a conformational change from $^1C_4$ to $^4C_1$ (Scheme 1). This conformational change is expected to be inhibited effectively in the levoglucosan–aromatic compound complex.

Table 1 summarizes the stabilization ability of various aromatic compounds as levoglucosan recovery under the experimental conditions of levoglucosan (10 mg)/aromatic compound (100 μL)/N_2/240 °C/15 min. Both stabilizing ability and levoglucosan solubility in the aromatic compound are quite different, depending on the chemical structure of aromatic compound. Both also have a tendency to be positively related to the π electron density. These results also support the hypothesis of the stabilizing mechanism through CH–π interaction, which is known to be enhanced with higher π-electron

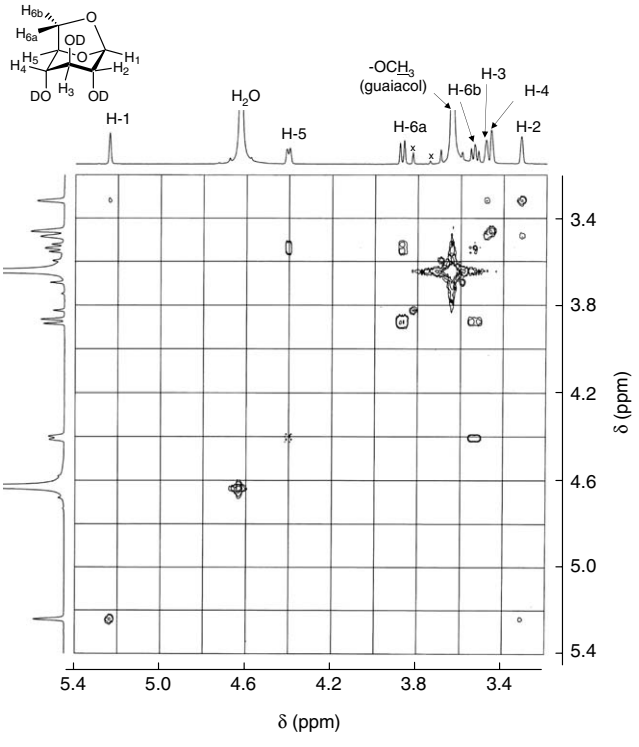


Figure 6. ^{1}H–^{1}H COSY spectrum (400 MHz) of a levoglucosan–guaiacol (15 mol equiv) mixture in D_2O: (×) derived from an impurity in guaiacol.

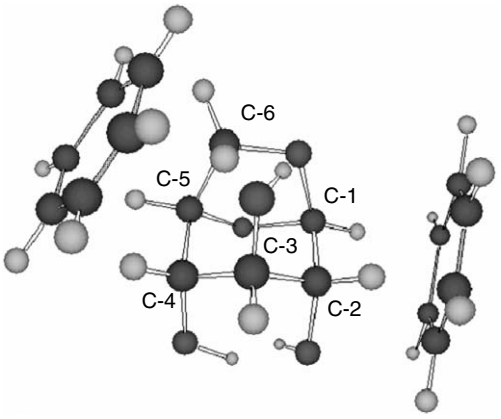
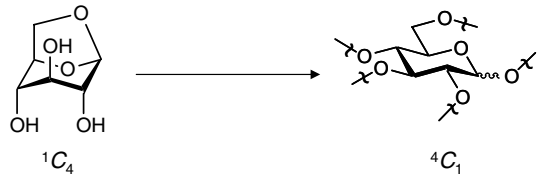
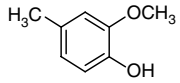
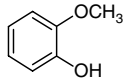
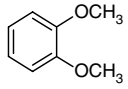
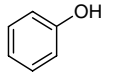
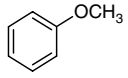
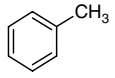
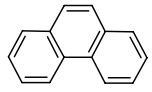


Figure 7. Levoglucosan–aromatic ring complexation indicated from the Δδ in the ^{1}H NMR analysis of a levoglucosan–guaiacol mixture in D_2O.



Scheme 1. Conformation change of levoglucosan in the ring-opening polymerization into polysaccharide.

Table 1. Solubility of levoglucosan in various aromatic compounds and levoglucosan recovery after heat treatment under the conditions of levoglucosan (10 mg)/aromatic compound (100 μL)/N_2/240 °C/15 min

Aromatic compound	Levoglucosan solubility	Levoglucosan recovery (%)
	++[a]	99.8
	++	96.9
	++	97.6
	++	96.4
	++	89.1
	+[b]	82.5
	+	87.6
	±[c]	33.5
	–[d]	8.3
	–	7.3

[a] Levoglucosan was completely dissolved.
[b] Levoglucosan was partially dissolved and gave a small amount of yellow-colored residue after heat treatment.
[c] Levoglucosan was partially dissolved and gave a substantial amount of dark-colored residue after heat treatment.
[d] Levoglucosan was not dissolved and gave a dark-colored residue after heat treatment.

density.[9,10,25–27] Low stabilization abilities of benzene, chlorobenzene and dichlorobenzene are conceivable with their low π-electron densities, which are not enough to form the stable levoglucosan–aromatic compound complexes.

The present results disclose the complexation of an anhydrosugar having $^1C_4$ conformation with the π-electrons of a benzene ring, and this information is expected to enhance our understanding of anhydrosugar chemistry related to its interaction with other substances. Furthermore, the present finding of the reduced thermal reactivity of the levoglucosan–aromatic complex will give useful information to control product selectivity in carbohydrate pyrolysis.

1. Experimental

1.1. Materials

Levoglucosan was purchased from Tokyo Kasei Co., and the other chemicals were purchased from Nacalai Tesque Co. as guaranteed grades.

1.2. Heat treatment and characterization of the products

Levoglucosan (10 mg) was heated in a closed Pyrex glass ampoule (internal diameter: 2.0 mm, length: 30 mm, thickness; 1.0 mm) under the conditions of N_2/240 °C/15 min with or without aromatic compounds (0.2–2.0 mol equiv to levoglucosan). After immediate cooling with cold water to quench the reaction, the ampoule was opened and extracted with distilled water (1.0 mL). The water-soluble portion was characterized by gel-permeation chromatography (GPC) using Shimadzu LC-10A under the chromatographic conditions: column—Shodex Asahipak GS-320 HQ + Asahipak GS-220 HQ; flow rate—0.6 mL min^{-1}; eluent—water; detector—RI; and temperature—30 °C. Levoglucosan recovery was also determined by gas chromatographic analysis (detector: flame ionization) of the water-soluble portion with *myo*-inositol as an internal standard after evaporating water in vacuo followed by trimethylsilylation with 2:1:7 (v/v/v) *N*,*O*-bis(trimethylsilyl)trifluoroacetamide–trimethylchlorosilane–pyridine using Shimadzu GC-18B under the following chromatographic conditions: column—Shimadzu CBP-5 (25 m × 0.25 mm∅); injector temperature—250 °C; column temperature—180 °C (1.0 min), 180→260 °C (1.0→9.0 min), 260 °C (9.0→19.0 min); carrier gas—helium; flow rate—1.5 mL min^{-1}.

1.3. ^{1}H NMR analysis

Levoglucosan (1.6 mg, 10 μmol) was dissolved in D_2O (1.0 mL) that included 1.2–18.6 mg (10–150 μmol) of guaiacol. After ultrasonic wave treatment for 10 min, the solution was used as the ^{1}H NMR sample. ^{1}H NMR analysis was conducted with a Bruker AC-400 (400 MHz) spectrometer: levoglucosan: δ 5.25 (s, 1H, H-1), 4.43 (m, 1H, H-5), 3.89 (dd, 1H, *J* 1.0, 7.7 Hz, H-6a), 3.56 (dd, 1H, *J* 5.8, 7.7 Hz, H-6b), 3.48 (m, 2H, H-3 and H-4), 3.33 (dd, 1H, *J* 1.6, 3.2 Hz, H-2).

References

1. Pictet, A. *Helv. Chim. Acta* **1918**, *1*, 226–230.
2. Wolfrom, M. L.; Thompson, A.; Ward, R. B. *J. Am. Chem. Soc.* **1959**, *81*, 4623–4625.
3. Wolfrom, M. L.; Thompson, A.; Ward, R. B.; Horton, D.; Moore, R. H. *J. Org. Chem.* **1961**, *26*, 4617–4620.
4. Shafizadeh, F.; Philpot, C. W.; Ostojic, N. *Carbohydr. Res.* **1971**, *16*, 279–287.

5. Schuerch, C. *Adv. Carbohydr. Chem. Biochem.* **1981**, *39*, 157–212.
6. Kawamoto, H.; Hatanaka, W.; Saka, S. *J. Anal. Appl. Pyrolysis* **2003**, *70*, 303–313.
7. Kawamoto, H.; Murayama, M.; Saka, S. *J. Wood Sci.* **2003**, *49*, 469–473.
8. Heyns, K.; Weyer, J. *Liebigs Ann. Chem.* **1968**, *718*, 224–237.
9. Nishio, M.; Hirota, M. *Tetrahedron* **1989**, *45*, 7201–7245.
10. Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. *Tetrahedron* **1995**, *51*, 8665–8701.
11. Nakai, Y.; Yamamoto, G.; Oki, M. *Chem. Lett.* **1987**, 89–92.
12. Kodama, Y.; Zushi, S.; Nishihata, K.; Nishio, M. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1306–1312.
13. Nakai, Y.; Inoue, K.; Yamamoto, G.; Oki, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2923–2931.
14. Iwamoto, H.; Takahashi, N.; Maeda, T.; Hidaka, Y.; Fukazawa, Y. *Tetrahedron Lett.* **2005**, *46*, 6839–6842.
15. Weis, W. I. *Annu. Rev. Biochem.* **1996**, *65*, 441–473.
16. Bazzicalupi, C.; Dapporto, P. *Struct. Chem.* **2004**, *15*, 259–268.
17. Re, S.; Nagase, S. *Chem. Commun. (Cambridge)* **2004**, 658–659.
18. Bernardi, A.; Arosio, D.; Potenza, D.; Sánchez-Medina, I.; Mari, S.; Cañada, F. J.; Jiménez-Barbero, J. *Chem. Eur. J.* **2004**, *10*, 4395–4406.
19. Spiwok, V.; Lipovová, P.; Skálová, T.; Buchtelová, E.; Hašek, J.; Králová, B. *Carbohydr. Res.* **2004**, *339*, 2275–2280.
20. Kobayashi, K.; Asakawa, Y.; Kato, Y.; Aoyama, Y. *J. Am. Chem. Soc.* **1992**, *114*, 10307–10313.
21. Kobayashi, K.; Ishii, K.; Sakamoto, S.; Shirasaka, T.; Yamaguchi, K. *J. Am. Chem. Soc.* **2003**, *125*, 10615–10624.
22. Kobayashi, K.; Asakawa, Y.; Kikuchi, Y.; Toi, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1993**, *115*, 2648–2654.
23. Tashiro, S.; Tominaga, M.; Kawano, M.; Therrien, B.; Ozeki, T.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 4546–4547.
24. Fernández-Alonso, M. del C.; Cañada, F. J.; Jiménez-Barbero, J.; Cuevas, G. *J. Am. Chem. Soc.* **2005**, *127*, 7379–7386.
25. Ehama, R.; Tsushima, M.; Yuzuri, T.; Suezawa, H.; Sakakibara, K.; Hirota, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 814–818.
26. Suezawa, H.; Hashimoto, T.; Tsuchinaga, K.; Yoshida, T.; Yuzuri, T.; Sakakibara, K.; Hirota, M.; Nishio, M. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1243–1249.
27. Hirota, M.; Sakakibara, K.; Suezawa, H.; Yuzuri, T.; Ankai, E.; Nishio, M. *J. Phys. Org. Chem.* **2000**, *13*, 620–623.
28. Hosoya, T.; Kawamoto, H.; Saka, S. *J. Anal. Appl. Pyrolysis*, submitted for publication.