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Inhibition of acid-catalyzed depolymerization of cellulose with boric acid in non-aqueous acidic media

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Abstract—Boric acid inhibited the acid-catalyzed depolymerization of cellulose in sulfolane, a non-aqueous medium, at high temperature. Formation of the dehydration products such as levoglucosenone, furfural, and 5-hydroxymethyl furfural were also effectively inhibited. Similar inhibition was observed for cellooligosaccharides and starch, although the glucosidic bonds in methyl glucopyranosides and methyl cellobioside were cleaved to form α-D-glucofuranose cyclic 1,2:3,5-bisborate.

Keywords: Cellulose; Starch; Acid-catalyzed depolymerization; Boric acid; Sugar borate; Cellooligosaccharide

1. Introduction

Cellulose is depolymerized in non-aqueous acidic media through an acid-catalyzed transglycosylation reaction.[1,2] Reduction in the degree of polymerization (DP) of cotton cellulose at 150–200 °C has been reported with $AlCl_3$ in CCl_4.[1] Addition of sulfuric acid has been reported to accelerate the cellulose depolymerization in sulfolane (tetramethylene sulfone) at 200 °C, and the depolymerized products were further converted to the dehydration products including levoglucosenone, furfural, and 5-hydroxymethyl furfural (5-HMF), along with colored substances.[2] Similar acid catalysis was also reported under pyrolysis conditions without using solvent.[3–5]

Cyclic borate or boronate ester formation is a well-known reaction of boric acid or boronic acid with the hydroxyl groups of a sugar, especially 1,2- and 1,3-*cis* diols.[6] The ester formation is usually conducted by heating the carbohydrate in an organic solvent such as benzene, 1,4-dioxane, pyridine, or *N*,*N*-dimethylformamide (DMF) with azeotropic removal of the water that is produced.[6] Such ester formation is also observed in aqueous alkaline media.[7–10] Although the pyranose, furanose and open-chain structures are possible for the esters of hexose, the furanose-type ester is known to form preferentially.[10–14]

As for glucose, α-D-glucofuranose cyclic 1,2:3,5-bis(phenylboronate) has been reported in heating with phenylboronic acid in organic solvent.[13–15] The ^1H and ^{13}C NMR spectra[13–15] and the X-ray crystal structure[15] have been reported for this boronate.

Kawamoto et al.[16] have reported that boric acid inhibited the formation of levoglucosenone, furfural, and 5-HMF in the heat treatment of levoglucosan (1,6-anhydro-β-D-glucopyranose) in 0.1% sulfuric acid–sulfolane at 200 °C through the formation of α-D-glucofuranose cyclic 1,2:3,5-bisborate (**1**). Phenylboronic acid also had a similar effect. Thus, sugar–borate (or boronate) ester was suggested to be fairly stable against acid-catalyzed reactions at high temperature. It is also interesting to know how such borate formation affects the polysaccharide reaction in nonaqueous acidic media at high temperature.

In this article, the influence of boric acid on the reactions of polysaccharides (cellulose and starch) and mono- and oligo-saccharides in acidic sulfolane is investigated.

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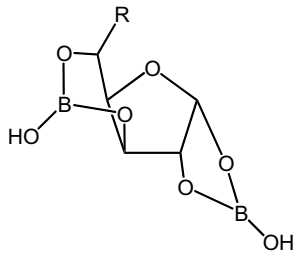

α-D-Glucofuranose cyclic 1,2:3,5-bisborate (R = -CH_2OH) (**1**)

α-D-Xylofuranose cyclic 1,2:3,5-bisborate (R = -H) (**2**)

2. Experimental

2.1. Materials

Cellulose powder (cotton, 200–300 mesh, Toyo Roshi Kaisha Ltd) and starch (corn, Nacalai Tesque Inc.) were used as polysaccharide samples. D-Glucose, D-xylose, D-cellobiose, methyl α-D-glucopyranoside, methyl β-D-glucopyranoside were purchased from Nacalai Tesque Inc. Cellopentaose and cellohexaose were obtained from Sigma–Aldrich Japan K.K. Methyl β-D-cellobioside was prepared from D-cellobiose by successive acetylation (Ac_2O/NaOAc/reflux), bromination (33% HBr in AcOH/AcOH/rt), methyl glycosylation (MeOH/Ag_2CO_3/molecular sieve/$CHCl_3$/rt) and deacetylation (28% NaOMe/MeOH/rt). Methyl 4-*O*-methyl β-D-glucopyranoside was prepared from methyl β-D-glucopyranoside via 4,6-benzylidene acetal formation (benzaldehyde dimethyl acetal/*p*-toluenesulfonic acid/DMF/50 °C/30 torr), benzylation (benzyl bromide/NaH/DMF/rt), reductive cleavage of the 4,6-benzylidene to the 6-*O*-benzyl derivative ($Et_3SiH/BF_3{\cdot}Et_2O/CHCl_3$/0 °C), methylation (MeI/NaH/DMF/rt) and debenzylation (10% Pd–C/H_2/MeOH/rt). Methyl 4-*O*-methyl β-D-cellobioside was also prepared from methyl β-D-cellobioside by a similar procedure. Silica gel plates (Kieselgel 60 F_{254}, Merck) were used for thin-layer chromatography (TLC). Other solvents and reagents were purchased from Nacalai Tesque Inc.

2.2. Heat treatment and characterization of the products

A sulfolane solution (1.0 mL) including 0.1% sulfuric acid and boric acid (3 mol equiv for the glucose unit) was added to cellulose (10 mg) in a Pyrex round-bottom flask (volume: 20 mL). The flask was attached with a condenser (a glass tube, 120 mm long and 14 mm in diameter) and a nitrogen bag through a three-way tap. After replacing the air in the reactor with nitrogen using an aspirator, the flask was heated in a silicon oil bath at 200 °C for 2 or 6 min. After the reaction, the reaction mixture was immediately cooled with flowing air (15 s) and subsequently by immersion of the flask in cold water (3 min). The mixture was filtered to give a residue and a colorless sulfolane-soluble portion. The sulfolane-soluble portion was neutralized with solid $NaHCO_3$ (50 mg) and analyzed by HPLC, GPC, and ^{1}H NMR spectroscopy as described in the following. The residue was sequentially washed with a satd aq $NaHCO_3$ solution and water, then dried at 105 °C for 24 h and weighed. In the repeated treatment experiment, the residue was treated again in a similar manner.

The sulfolane-soluble portion was mixed with a solution of *p*-dibromobenzene (an internal standard, 4.0 mg) in tetrahydrofuran (THF, 1.0 mL), and the resulting solution was analyzed by HPLC using a Shimadzu LC-10A under the following conditions: column, STR ODS-II; flow rate, 1.0 mL min^{-1}; eluent, 20:80 MeOH–H_2O (5 min), 20:80→30:70 (5 min), 30:70→100:0 (8 min); detector, UV_{220nm}; column temperature, 40 °C; retention times, 5-HMF, 5.6 min; levoglucosenone, 6.2 min; furfural, 6.7 min.

GPC analysis was conducted for the sulfolane-soluble portion after dilution with a 4-fold volume of THF with a Shimadzu LC-10A. The chromatographic conditions were as follows: column, Shodex KF801 + KF802; flow rate, 1.0 mL min^{-1}; eluent, THF; detector, RID; column temperature, 40 °C.

Since the borate ester was unstable during the working up process, the reaction mixture was directly analyzed by ^{1}H NMR spectroscopy. The sulfolane-soluble portion (0.15 mL) was mixed with $CDCl_3$ or dimethyl sulfoxide (DMSO-d_6, 0.45 mL) with *p*-dibromobenzene as an internal standard, and the resulting solution was analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra were recorded with a Varian AC-400 (400 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and coupling constants (J) are given in ppm and Hz, respectively.

Starch and other model compounds were also treated in a similar manner.

3. Results and discussion

3.1. Cellulose

Figure 1 shows pictures of the solutions and residue obtained from the 6-min heating of cellulose in 0.1% sulfuric acid–sulfolane at 200 °C in the presence and the absence of boric acid (3 mol equiv against the glucose-repeating unit in cellulose). The residue recoveries are also included. In the absence of boric acid, cellulose was completely converted to the sulfolane-soluble products, along with a change in the color of the solution to dark reddish-brown. As listed in Table 1, levoglucosenone (24.8 mol %), furfural (8.0 mol %), and 5-HMF (2.7 mol %) (based on the glucose unit) were obtained as the identified products. These results are consistent with the results of the previous work.[2] The boric acid

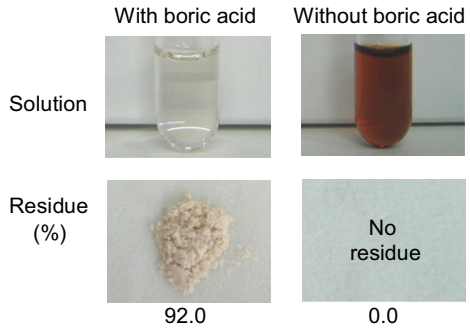

Figure 1. Influence of the boric acid addition on the decomposition of cellulose in 0.1% sulfuric acid/sulfolane (N_2/200 °C/6 min). Boric acid/glucose unit in cellulose = 3:1 (mol/mol).

Table 1. Influence of the boric acid addition on the yields of levoglucosenone, furfural, and 5-HMF in heat treatment of cellulose in 0.1% sulfuric acid/sulfolane (N_2/200 °C/6 min)

	Yield (mol %)	
	With boric acid[a]	Without boric acid
Levoglucosenone	0.2	24.8
Furfural	0.2	8.0
5-HMF	0.1	2.7
Total	0.5	35.5

[a] Boric acid/glucose unit in cellulose = 3:1 (mol/mol).

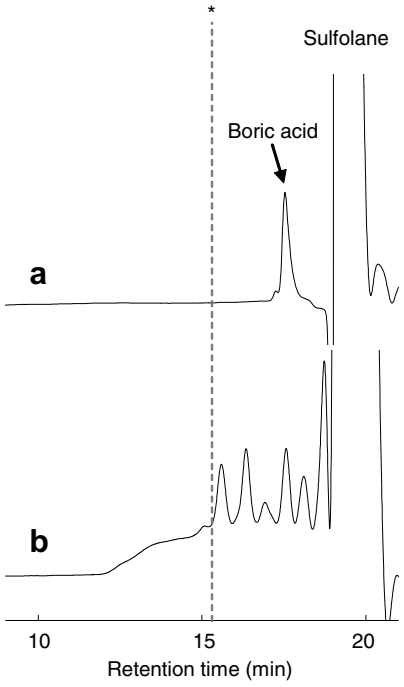

Figure 2. GPC chromatograms of the sulfolane-soluble portions after heat treatment of cellulose in 0.1% sulfuric acid/sulfolane in the presence (a) and the absence (b) of boric acid (N_2/200 °C/6 min). Boric acid/glucose unit in cellulose = 3:1 (mol/mol), * retention time of α-D-glucofuranose cyclic 1,2:3,5-bisborate.

addition substantially changed such reaction behavior of cellulose. Solubilization of cellulose and colored substance formation were almost completely inhibited in the presence of boric acid. Filtration gave a cream-colored residue (92.0%) and a colorless sulfolane-soluble portion. Furthermore, the formation of levoglucosenone, furfural, and 5-HMF were also substantially inhibited (total yield: 0.5%). Thus, the boric acid addition inhibited the acid-catalyzed depolymerization of cellulose and further decomposition into dehydration products.

Figure 2 shows the GPC chromatograms of these sulfolane-soluble portions. In the absence of boric acid (chromatogram b), several peaks, including a broad signal in the higher molecular weight (MW) region, are observed. Contrary to this, only the boric acid peak is observed in the presence of boric acid (chromatogram a), and the signal corresponding to α-D-glucofuranose cyclic 1,2:3,5-bisborate (**1**, retention time: 15.5 min) is not observed at all. From the ^{1}H NMR signal (6.5 ppm) assigned to the B-OH [sulfolane-soluble portion/dimethylsulfoxide (DMSO)-d_6 = 1/3, v/v], more than 80% of the boric acid used was found to be recovered. Since the formation of glucose borate **1** requires 2 mol equiv of boric acid, a large part of the boric acid remains unreacted with the cellulose.

The residue obtained from the heat treatment of cellulose in the presence of boric acid was further treated under the similar conditions. The cellulose recoveries and glucose yields, which were determined by the GC analysis of the alditol acetates prepared from the water extracts of the residues are listed in Table 2. In this repeated treatment, 1st and 2nd cycles showed very similar results. About 10% (1st cycle: 8.0%, 2nd cycle: 10.6%) of the amount of the cellulose used were removed after each treatment. These results and high boric acid recovery indicate that only the cellulose molecules near the surface area are reactive with boric acid under these conditions. These molecules would depolymerize to the low-MW products, which are further converted to the borate complexes. About 10% of the cellulose would be converted to such borate complexes and removed as soluble substances during washing with water. Low yields of glucose (1st cycle: 0.023%, 2nd cycle: 0.032%) indicate that these molecules are not depolymerized up to the monomer level. The cellulose molecules covered with the borate

Table 2. Cellulose recovery (%) and glucose yield (mol %) in the repeated heat treatment of cellulose in 0.1% sulfuric acid/sulfolane in the presence of boric acid (boric acid/glucose unit in cellulose = 3:1, mol/mol) (N_2/200 °C/6 min)

	Cellulose recovery (%)	Glucose yield (mol %)
First cycle	92.0	0.023
Second cycle	89.4[a]	0.032[a]

[a] Based on the amount used in the second cycle.

complex layer would be stabilized against the acid-catalyzed transglycosylation.

These results are totally different from the previous results with levoglucosan. Under similar reaction conditions, the C-1–O bond of levoglucosan was completely cleaved through acid-catalyzed transglycosylation and gave α-D-glucofuranose cyclic 1,2:3,5-bisborate **1** in 71.5 mol % yield.

3.2. Model compounds

To investigate the origin of the different behaviors between cellulose and levoglucosan in more detail, various low-MW model compounds and starch (listed in Table 3) were treated under similar conditions. The ^{1}H NMR spectra (sulfolane-soluble portion/DMSO-d_6 or $CDCl_3 = 3/1$, v/v) are shown in Figures 3 and 4. Table 3 summarizes the reaction behavior (solubilization, color of solution) and the yields of borate, furfural, 5-HMF, and levoglucosenone along with the solubility of the model compounds in sulfolane. Starch, a polysaccharide, exhibited the cellulose-type behavior. The influences of boric acid on the model compounds varied depending on their structures.

As for the reducing sugars (Fig. 3), the DP determined whether the influence is of the cellulose- or levoglucosan type. Glucose and cellobiose formed α-D-glucofuranose cyclic 1,2:3,5-bisborate (**1**) in 85.1 and 71.9 mol % yields (based on the glucose unit), respectively, and the formation of the dehydration products and colored substances were completely inhibited (levoglucosan-type). Xylose also showed similar results. From the ^{1}H NMR spectrum (Fig. 3), α-D-xylofuranose cyclic 1,2:3,5-bisborate (**2**) was suggested to form in 92.9 mol % yield. The structure was confirmed by comparing the ^{1}H NMR spectrum with that of α-D-xylofuranose cyclic 1,2:3,5-bis(phenylboronate) from the literature.[17] Glucose borate **1** and xylose borate **2** were fairly stable during heat treatment in acidic sulfolane. High yields of these esters also indicate that the OH-6 in glucose borate **1** does not influence its stability.

Contrary to these results, cellopentaose and cellohexaose showed the cellulose-type behavior. These compounds were recovered as cream-colored substances with colorless sulfolane solutions.

Methyl α- and β-D-glucosides, methyl β-D-cellobioside exhibited the similar results (levoglucosan-type behavior) to those of glucose and cellobiose. After acid-catalyzed glycosidic bond cleavage, similar borate formation would occur as observed for the reducing sugars. Methyl 4-*O*-methyl-β-D-glucopyranoside and methyl 4′-*O*-methyl-β-D-cellobioside gave colored sulfolane-soluble portions, which indicated the progress of some degradation reactions. The ^{1}H NMR signals assigned to levoglucosenone (□), furfural (○), and 5-HMF (△) are observed in these compounds, and their total yields were 16.8 and 15.2 mol % (based on the glucose unit), respectively. These two NMR spectra are very similar except for the large signals (●) assigned to glucose borate **1** in the spectrum from 4′-*O*-methyl-β-D-cellobioside. Glucose borate **1** is considered to arise from the glucose unit without a 4-*O*-methyl group. This

Table 3. Reactivities of various sugars in acidic sulfolane with boric acid at 200 °C [boric acid (3 mol equiv for the monosaccharide-unit)/0.1% sulfuric acid/sulfolane/N_2/2 min]

	Solubility in sulfolane (20 °C)[a]	Reaction behavior		Yield[d] (mol %)			
		Solubilization[b]	Color of solution[c]	Borate	Furfural	5-HMF	Levoglucosenone
D-Glucose	△	○	−	85.1[e]	—[g]	—	—
D-Xylose	△	○	−	92.9[f]	Trace	—	—
D-Cellobiose	△	○	−	71.9[e]	—	—	—
Cellopentaose	×	×	−	—	—	—	—
Cellohexaose	×	×	−	—	—	—	—
Methyl β-D-glucopyranoside	○	○	−	68.9[e]	—	—	—
Methyl α-D-glucopyranoside	○	○	−	79.8[e]	—	—	—
Methyl β-D-cellobioside	○	○	−	59.6[e]	—	—	—
Levoglucosan	○	○	−	71.5[e]	—	—	—
Methyl 4-*O*-methyl-β-D-glucopyranoside	○	○	+	—	5.0	9.5	2.3
Methyl 4′-*O*-methyl-β-D-cellobioside	○	○	+	36.6[e]	5.0	6.7	3.5
Cellulose	×	×	−	—	—	—	—
Starch	×	×	−	—	—	—	—

[a] ○: soluble, △: partially soluble, ×: insoluble.
[b] ○: solubilized, ×: not solubilized.
[c] +: dark reddish brown, −: colorless.
[d] Based on the monosaccharide unit.
[e] α-D-Glucofuranose cyclic 1,2:3,5-bisborate.
[f] α-D-Xylofuranose cyclic 1,2:3,5-bisborate.
[g] Not detectable.

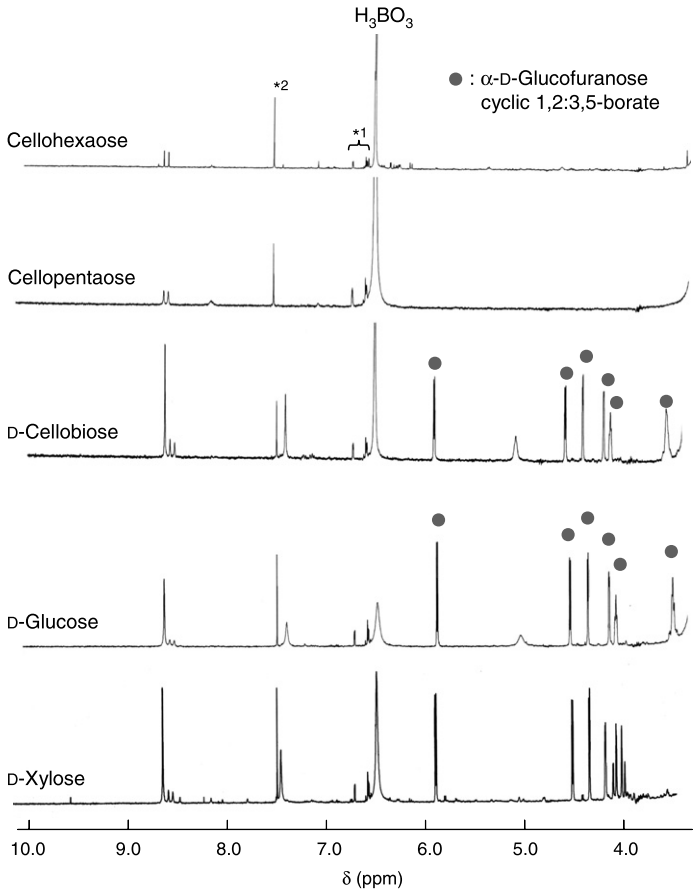

Figure 3. ^{1}H NMR spectra of the sulfolane-soluble portions obtained from some reducing sugars [boric acid (3 mol equiv for the monosaccharide-unit)/0.1% sulfuric acid/sulfolane/N_2/200 °C/2 min, sulfolane-soluble portion /DMSO-d_6 = 1/3, v/v]. *1 Impurity in sulfolane, *2 internal standard (*p*-dibromobenzene).

is also supported from the yield (36.6 mol %), which is almost half of that (71.9 mol %) from cellobiose. The 4-*O*-methyl glucose unit would further decompose to dehydration products and colored substances.

Decomposition of the 4-*O*-methylated glucose-moiety is explained with difficulty in the stable borate ester formation. Foster[18] compared the borate complexation of various methylated glucoses in aqueous alkaline media and reported that methylation of the OH-1, OH-2, or OH-4 substantially reduced the complexation ability, while the influence of the methylation of OH-3 or OH-6 was small. The 4-O-methylation inhibits the formation of the glucofuranose-type structure. Preferential formation of the furanose-type esters has been reported in the literature.[10–14]

3.3. Mechanism

Based on the present results, the origin of the different actions of boric acid on sugar is discussed with a proposed mechanism shown as in Figure 5. As shown in Table 3, the solubility of the sugar in sulfolane varied depending on the sugar type. Such solubility differences would be important in the reaction behavior in acidic sulfolane with boric acid. Soluble sugar undergoes the acid-catalyzed transglycosylation to form the monosaccharide borate (pathway a). The following reaction behavior depends on the stability of the borate complex. The less-stable complex (e.g., 4-*O*-methyl derivatives) further decomposes to the products including levoglucosenone, furfural, 5-HMF, and colored substances, while the stable complex remains unreacted in the solution.

As for the insoluble sugar, pathway a becomes competitive with the reaction with boric acid at the surface molecules (pathway b). When the reactivity is a > b, sugar is converted to the soluble borate complex (glucose, xylose, and cellobiose). In the case of the reactivity a < b, the sugar particle is covered with the borate complexes, and these serve as a protective layer for the inner sugar molecules against the acid-catalyzed transglycosyl- ation and other degradation reactions (cellopentaose, cellohexaose, cellulose, and starch), although the protection mechanism of the coated layer is not known at the moment.

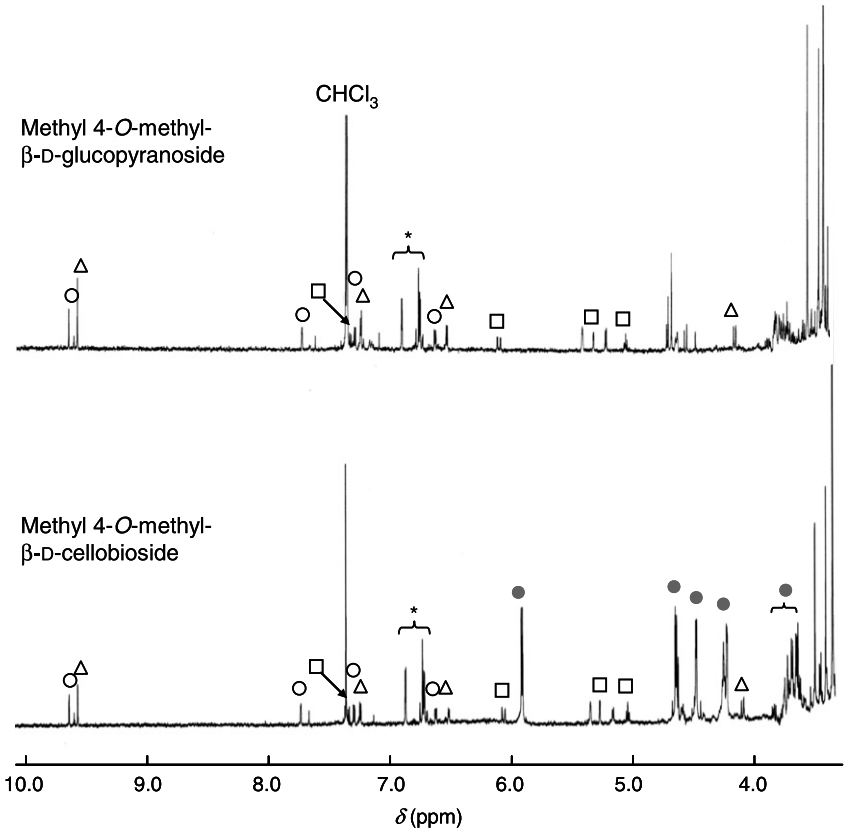

Figure 4. ^{1}H NMR spectra of the sulfolane-soluble portions obtained from methyl 4-*O*-methyl-β-D-glucopyranoside and methyl 4′-*O*-methyl-β-D-cellobioside [boric acid (3 mol equiv for the monosaccharide-unit)/sulfolane/N_2/200 °C/2 min, sulfolane-soluble portion/$CDCl_3$ = 1/3, v/v]. ∗Impurity in sulfolane, ○: furfural, △: 5-HMF, □: levoglucosenone, ●: α-D-glucofuranose cyclic 1,2:3,5-bisborate.

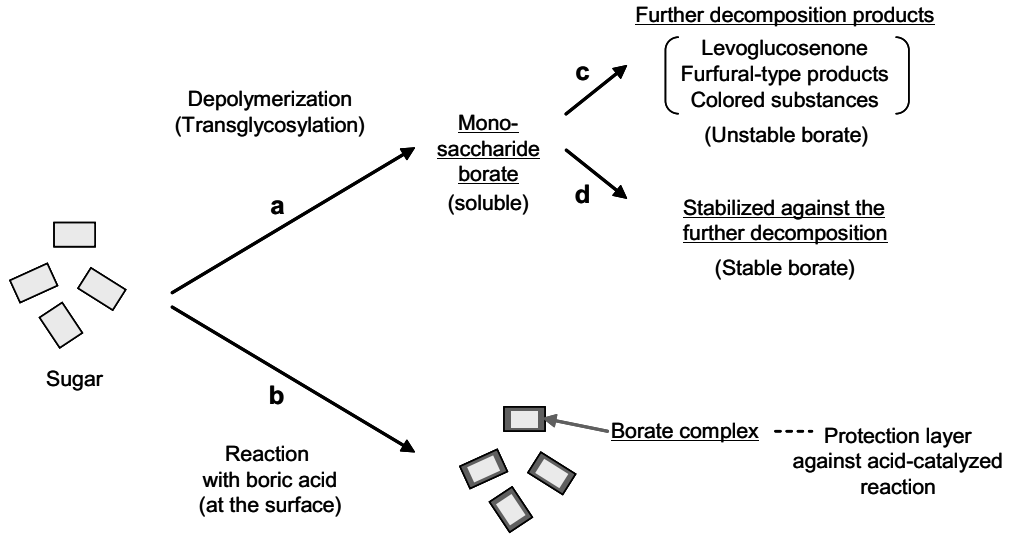

Figure 5. A proposed mechanism for the different actions of boric acid on sugar under heat treatment in non-aqueous acidic media at high temperature.

Acknowledgments

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