

Effect of stereo-configurational difference of carbohydrate model compound on the reaction with active oxygen species under oxygen delignification conditions

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Abstract We examined how the stereo-configurational difference affects the reaction of a carbohydrate model compound with active oxygen species (AOS) generated in situ by reactions between O₂ and a phenolic compound under conditions similar to those of oxygen delignification or with oxyl anion radical, the conjugate base of hydroxyl radical, generated by the decomposition of H₂O₂ under alkaline conditions. As the phenolic compound, 2,4,6-trimethylphenol or 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol) was used. The carbohydrate model compounds employed were methyl β-D-glucopyranoside (MGPβ) and its 4 epimers, methyl α-D-glucopyranoside (MGPα), methyl β-D-mannopyranoside (MMP), methyl β-D-allopyranoside (MAP), and methyl β-D-galactopyranoside (MGaP). Their stabilities were in the order of MGPα > MGPβ > MMP > MGaP > MAP, indicating that the reactivity of the carbohydrate model compound is significantly dependent on where the stereo-configurational difference is. Only the co-existence of MMP enhanced the degradation of MGPβ, when a pair of MGPβ and another carbohydrate model compound was reacted with the AOS. This result suggests that the profile of AOS in the system is dependent not only on the type of phenolic compound, the

generator of AOS, but also on that of the carbohydrate model compound.

Keywords Bleaching · Cellulose · Hydrogen peroxide · Lignin · Pulp

Introduction

It is still a serious problem that oxygen delignification is accompanied by severe damage to carbohydrates. The degradation of carbohydrates is not caused by direct attack of O₂ but by active oxygen species (AOS) generated in situ by reactions between O₂ and phenolic units in lignin [1–5]. We have studied the fundamental chemistry of oxygen delignification since the 1990s. It has been a recent topic of this fundamental chemistry which position of carbohydrate model compound is preferentially attacked by AOS under conditions of oxygen delignification [6–10].

As another topic, we partially examined the effect of stereo-configurational differences of a carbohydrate model compound on the reaction with AOS generated in situ by reactions between O₂ and a phenolic compound, 2,4,6-trimethylphenol (TMPh, Fig. 1) or 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol, Valc, Fig. 1), under conditions similar to those of practical oxygen delignification, and published several reports [6–8]. In these reports, a pair of a carbohydrate model compound, methyl β-D-glucopyranoside (MGPβ, Fig. 1), and an epimer, methyl α-D-glucopyranoside (MGPα, Fig. 1) or methyl β-D-mannopyranoside (MMP, Fig. 1), was reacted with the AOS under the specified conditions [6–8]. The degradation of MGPβ is greater or less than that of MGPα or MMP, respectively, when each of 2 pairs is reacted with the AOS (Fig. 2) [6–8]. These results indicate that the effect of the

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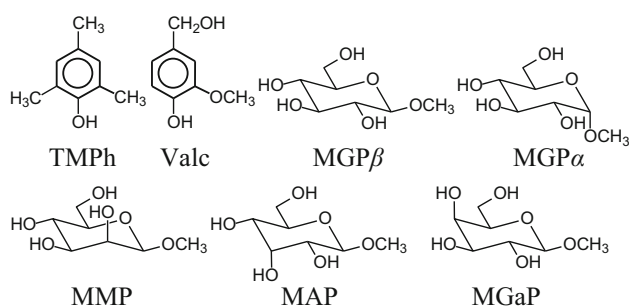


Fig. 1 Chemical structure of the phenolic and carbohydrate model compounds employed in this study

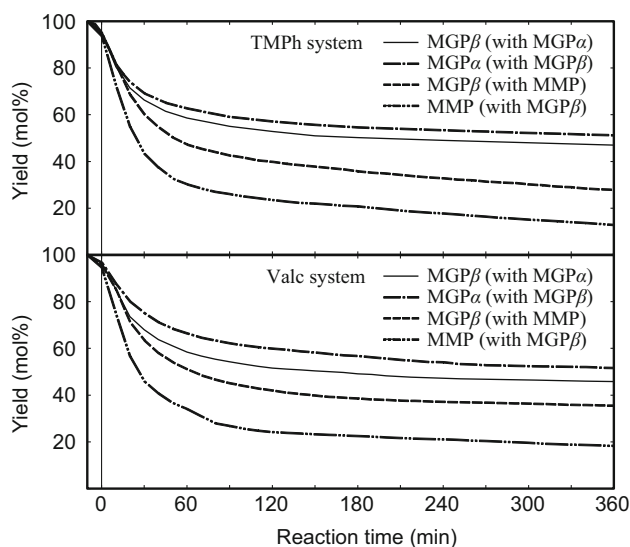


Fig. 2 Change in the yields of MGPβ, MGPα, and MMP when a pair of MGPβ and MGPα or of MGPβ and MMP was subjected to the oxygen-alkali treatment in the presence of TMPH (*upper*) or Valc (*lower*) in our previous reports [6–8] (the best-fit curves are shown. Refer to the literatures [6–8] for the actual data points)

stereo-configurational difference on the reaction with the AOS is dependent on where the stereo-configurational difference is.

In this paper, we further examined how the stereo-configurational difference of the carbohydrate model compound affects the reaction with AOS under conditions of oxygen delignification. A carbohydrate model compound, MGPβ, MGPα, MMP, methyl β-D-allopyranoside (MAP, Fig. 1), or methyl β-D-galactopyranoside (MGaP, Fig. 1), or a pair of MGPβ and one of these compounds was reacted with AOS generated in situ by reactions between O₂ and a phenolic compound, TMPH or Valc, under the same oxygen delignification conditions as those employed in our previous studies [6–8] or with oxyl anion radical (O^{•−}), the conjugate base of hydroxyl radical (HO[•]), generated by the decomposition of H₂O₂ under the same alkaline conditions as those employed in our previous reports [6–8]. In the

alkaline H₂O₂ treatment, O^{•−} is the only AOS that can attack and degrade the carbohydrate model compound [6–8].

Materials and methods

Materials

Semiconductor grades (99.99+ %) of NaOH and FeCl₃ (Sigma-Aldrich Japan K. K., Tokyo, Japan), an H₂O₂ solution (30 %) containing no stabilizer, and all the other chemicals used in this paper were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan or Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. All the chemicals were used without further purification except for the carbohydrate model compounds. Ultra-high-purity water (Puric-Z, Organo Co., Tokyo, Japan) was used in all the experiments.

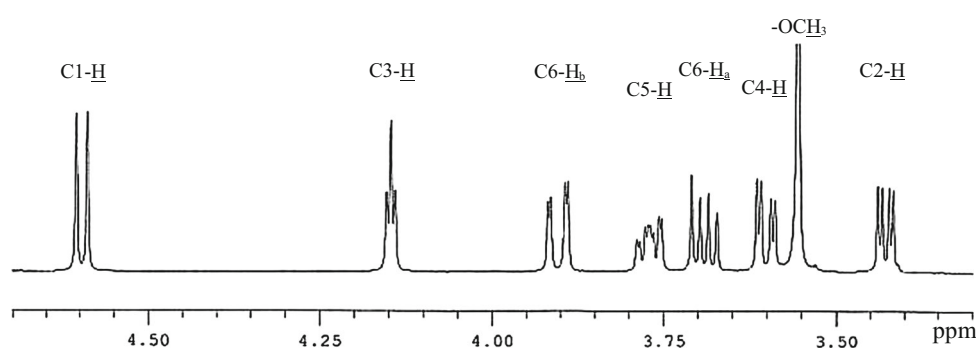
MGPβ and the epimers at the anomeric, C-2, C-3, and C-4 positions, MGPα, MMP, MAP, and MGaP, respectively, were used as carbohydrate model compounds in this paper. MGPβ, MGPα, and MGaP were purchased from Wako Pure Chemical Industries, Ltd. or Tokyo Chemical Industry Co., Ltd., and used after recrystallization. MMP was purchased from Toronto Research Chemicals Inc. (North York, ON, Canada) as the hemi-isopropylate. The removal of isopropyl alcohol was described in our previous report [7].

MAP was synthesized from MGPβ according to the method of Weinges et al. [11]. Diethyl azodicarboxylate was slowly added to THF containing MGPβ, triphenylphosphane, and benzoic acid, and the mixture was maintained at 60 °C for 1 h with stirring to undergo the Mitsunobu reaction. The obtained syrup consisting mainly of methyl 3-*O*-benzoyl-β-D-allopyranoside was added to a NaOCH₃/CH₃OH solution for the debenzoylation, followed by desalination using a cation exchange resin and a strong base anion exchange resin in this order. The yield was 35 % after purification. The structure and purity of MAP were confirmed by ¹H-NMR (JNM-A500, 500 MHz, JEOL Ltd.) (Fig. 3) ¹H-NMR (D₂O): δ 3.41–3.44 (dd, 1H, *J* = 3.0, *J* = 8.0, C2-H), 3.54–3.57 (s, 3H, -OCH₃), 3.58–3.62 (dd, 1H, *J* = 3.0, *J* = 10.0, C4-H), 3.67–3.72 (dd, 1H, *J* = 6.0, *J* = 12.0, C6-H_a), 3.75–3.79 (m, 1H, C5-H), 3.88–3.92 (dd, 1H, *J* = 2.0, *J* = 12.0, C6-H_b), 4.13–4.16 (dd, 1H, *J* = 3.0, *J* = 3.0, C3-H), 4.58–4.62 (d, 1H, *J* = 8.0, C1-H).

Oxygen-alkali treatment

A reaction solution (300 mL) was prepared to contain NaOH (0.50 mol/L), FeCl₃ (0.36 mmol/L), TMPH or Valc

Fig. 3 $^1\text{H-NMR}$ spectrum of MAP



as a phenolic compound (0 or 9.0 mmol/L), and 1 or 2 carbohydrate model compound(s) [4.0 mmol/L (each)]. The solution was transferred into a Teflon-coated stainless steel vessel (500 mL, Taiatsu Techno[®] Co., Tokyo, Japan), and O₂ (or N₂) was added to a pressure of 1.1 MPa (1.0 MPa as the gauge level). The vessel was heated to 95 °C for 10 min, which was maintained for 360 min with stirring. The reaction time was defined as 0 when the temperature reached 95 °C. At prescribed times, a portion of the solution was withdrawn for quantification of the residual carbohydrate model and phenolic compounds.

The reaction system using TMPH or Valc is described as “the TMPH or Valc system.” respectively, in this paper.

Alkaline hydrogen peroxide treatment

A reaction solution (29.8 mL) was prepared to contain NaOH (0.50 mol/L), FeCl₃ (0.36 mmol/L), and a carbohydrate model compound, MGPβ, MGPα, MMP, MAP, or MGaP (4.0 mmol/L). The solution was transferred into a Teflon vessel (50 mL) and heated to 95 °C in a bath containing saturated NaCl solution. A H₂O₂ solution (30 %, 0.2 mL) was added to the vessel to initiate the reaction, and the reaction time at this moment was defined as 0. The initial concentration of H₂O₂ was 58.8 mmol/L. At prescribed times, a portion of the reaction solution was withdrawn to quantify the carbohydrate model compounds. The withdrawn solution was primarily reacted with NaBH₄ at room temperature for 30 min to quench possibly residual H₂O₂.

The reaction system is described as “the H₂O₂ system” in this paper.

Quantification of carbohydrate model and phenolic compounds

The work-up and analytical procedures for quantification of the residual carbohydrate model and phenolic compounds were as described in our previous reports [6–8]. Basically, the residual carbohydrate model compounds and

Valc were quantified by GC as the acetyl derivatives with the internal standard compound (*myo*-inositol). TMPH was separately quantified by GC with the internal standard compound (4-chlorophenol) as the dichloromethane extracts.

Results and discussion

Stability of carbohydrate model compound in the absence of phenolic compound

As described in the introduction, O₂ does not directly attack carbohydrates, but AOS generated in situ by reactions between O₂ and the phenolic units in lignin mainly attack and degrade them in an oxygen delignification process. To confirm the stability of the carbohydrate model compounds in the absence of a phenolic compound, MGPβ, MGPα, MMP, MAP, or MGaP was subjected to the oxygen-alkali treatment as a sole carbohydrate model compound without the addition of phenolic compound (Table 1). MGPβ, MGPα, MAP, and MGaP were almost stable but MMP was slightly degraded. We observed, on the other hand, that MMP was stable in the nitrogen-alkali treatment under otherwise the same conditions as those of the oxygen-alkali treatment (Table 1). We suggest, therefore, that MMP is attacked directly by O₂ or degraded by radical chain-type reactions initiated by some tiny amounts of AOS generated from unknown contaminants more easily than the others. Because the degradation of MMP was not

Table 1 List of the yield of each carbohydrate model compound at a reaction time of 360 min when solely subjected to the oxygen-alkali treatment without the addition of phenolic compound

Yield (mol %)					
MGPβ	MGPα	MMP	MAP	MGaP	MMP ^a
96.7	96.5	91.2	99.0	102.3	103.1

^a Nitrogen-alkali treatment

great, however, we can state that the degradation of the carbohydrate model compounds observed in this paper was caused by the attack of AOS in the TMPH and Valc systems or by $O^{\bullet-}$ in the H_2O_2 system.

Reaction of single carbohydrate model compound with AOS

Figure 4 illustrates the degradation of MGP β , MGP α , MMP, MAP, or MGaP, when each compound was treated as a sole carbohydrate model compound in the TMPH system. The degradation of TMPH almost always showed the same behavior in any reaction, as shown in Fig. 5 in which a pair of MGP β and MAP was treated. TMPH always disappeared from the system at a reaction time of about 45 min. The degradation of any carbohydrate model compound was severe in the early stage of the reaction where TMPH still existed, and gradually became moderate after this period. The degrees of the degradations were in increasing order of MGP α < MGP β < MMP < MGaP < MAP (Fig. 4). The degradation of MAP was especially great. The degrees seem to be roughly categorized into three groups, MGP β and MGP α , MMP and MGaP, and only MAP, which may suggest that the orientation of their three secondary hydroxy groups is a determining factor for the degree of degradation. MGP β and MGP α , which are relatively more stable, have three equatorially oriented secondary hydroxy groups, and the orientational relationships between the C-2 and C-3 and between the C-3 and C-4 hydroxy groups are *trans*. MMP and MGaP have two equatorially and one axially oriented secondary hydroxy groups, and the orientational relationships between the C-2 and C-3 and between the C-3 and C-4 hydroxy groups are *cis* and *trans* in MMP, respectively, and *trans* and *cis* in MGaP, respectively. MAP also has two equatorially and

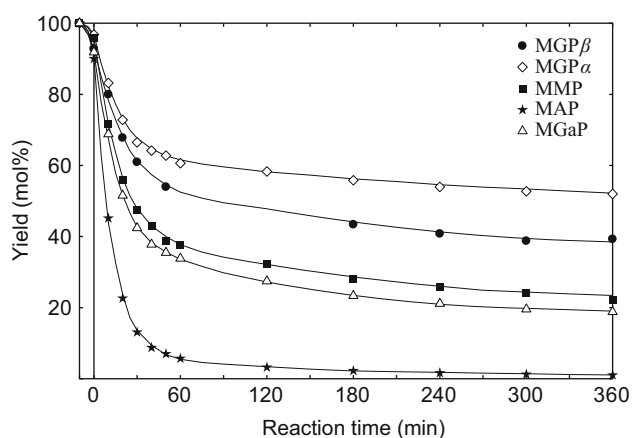


Fig. 4 Change in the yields of MGP β , MGP α , MMP, MAP, and MGaP when each was subjected to the TMPH system as a sole carbohydrate model compound

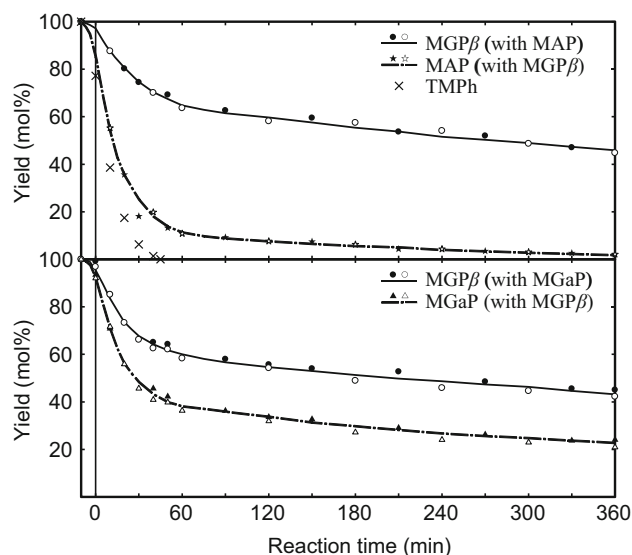


Fig. 5 Change in the yields of MGP β , MAP, and MGaP when a pair of MGP β and MAP (*upper*) or of MGP β and MGaP (*lower*) was subjected to the TMPH system

one axially oriented secondary hydroxy groups, but both orientational relationships are *cis*. The presence of *cis*-related orientation in two neighboring secondary hydroxy groups may make the carbohydrate model compound vulnerable to attack by AOS. It was previously reported that the degradation of methyl β -D-ribofuranoside was greater than that of methyl β -D-xylofuranoside when each compound was treated as a sole organic compound under conditions similar to but severer than those employed in this study and hence the model compound was degraded by AOS generated by chain-type reactions during a prolonged period of time [12]. It was suggested in this report that the *cis*-related orientation between the C-2 and C-3 hydroxy groups in the former compound results in the degradation severer than the latter compound. The lower stability of MGP β compared with MGP α should be dependent on the higher thermodynamic stability of the latter due to the anomeric effect.

Table 2 lists the yields of the carbohydrate model compounds, when each of them was treated in the H_2O_2 system as a sole carbohydrate model compound. In this system, the decomposition of H_2O_2 generates $O^{\bullet-}$ and $O_2^{\bullet-}$, and the former is the only AOS that can attack the

Table 2 List of the yield of each carbohydrate model compound at a reaction time of 15 min when solely subjected to the H_2O_2 system

Yield (mol %)				
MGP β	MGP α	MMP	MAP	MGaP
51.1	57.9	26.4	0.2	18.6

carbohydrate model compound. A relatively large amount of H_2O_2 was added (58.8 mmol/L). The requirement for the large amount was explained in our previous report [13]. H_2O_2 disappeared from the system before a reaction time of 5 min, which was confirmed by iodometric titration. No epimeric methyl glycopyranoside was produced by the post-reduction of each withdrawn solution with NaBH_4 to quench possibly residual H_2O_2 . This result indicates that the primary degradation products of the carbohydrate model compounds, which should have a carbonyl group at a position, are significantly labile under alkaline conditions as those employed in this study and instantaneously converted to further degradation products. This instantaneous conversion should also occur in the oxygen-alkali treatment. Degradation of the carbohydrate model compounds occurred until this time, and their yields were almost constant after this time. The degradability of carbohydrate model compounds was in the same order as with the TMPH system. The degradation of MAP was also especially great. This order can correspond to that of the vulnerability of these carbohydrate model compounds to attack by $\text{O}^{\bullet-}$ because the reaction was conducted in air and hence their degradations caused by chain-type reactions should be negligible. This result suggests that $\text{O}^{\bullet-}$ operates as a main AOS in the TMPH system, although the generation of some AOS specific only to the TMPH system was proposed in our previous reports [9, 10]. In biological systems, it was indicated that D-allose has a potent inhibitory effect on the production of AOS from stimulated neutrophils [14]. Although this inhibitory effect does not originate from an alloside but from the mother D-allose, it is indicated here that an alloside, MAP, also has a relatively high scavenging effect on AOS in the purely chemical TMPH and H_2O_2 systems.

Reaction of a pair of MGP β and another carbohydrate model compound with AOS

To examine the effect of a co-existing carbohydrate model compound, a pair of MGP β and another carbohydrate model compound was reacted in the TMPH or Valc system. Figures 5 and 6 show the degradations of TMPH and Valc, respectively, in the reaction of a pair of MGP β and MAP. The degradation of TMPH was always as described in the previous section. The degradation of Valc was always the same in any reaction. Valc always disappeared from the system at a reaction time of about 60 min, which indicates that Valc is slightly more resistant to the O_2 oxidation than TMPH in accordance with our previous reports [8–10, 15]. The degradation of any carbohydrate model compound was severe in the early stage of the reaction when Valc still existed, and gradually became moderate after this period. Especially, the degradation of MAP was greater than that

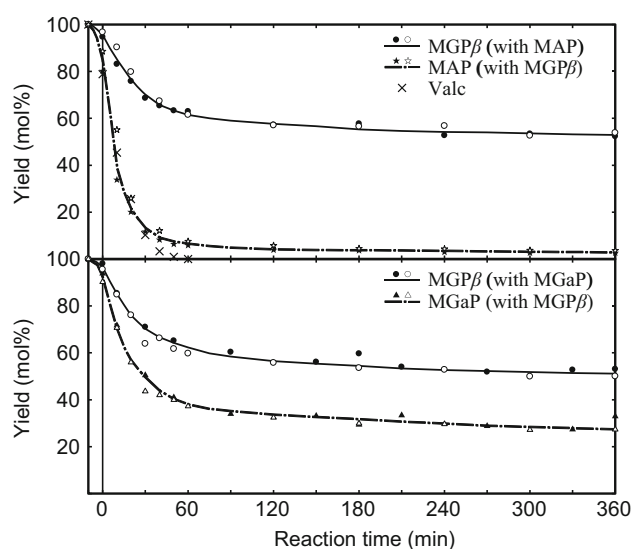


Fig. 6 Change in the yields of MGP β , MAP, and MGaP when a pair of MGP β and MAP (*upper*) or of MGP β and MGaP (*lower*) was subjected to the Valc system

of Valc, the generator of AOS, in the early period. This result may indicate that MAP is degraded not only by AOS generated readily by reactions between O_2 and Valc but also by those generated as intermediates of chain-type reactions, although the chain-type reaction should not propagate significantly owing to the scavenging effect of Valc.

The data for the reactions of two pairs of MGP β and MGP α and of MGP β and MMP are from our previous reports (Fig. 1) [6–8]. Figures 5 and 6 illustrate the degradations of the carbohydrate model compounds when a pair of MGP β and MAP or of MGP β and MGaP was treated in the TMPH or Valc system, respectively. Figure 7 is created by combining the data illustrated in Figs. 4 and 5, and shows the degradation of MGP β in the TMPH system, when MGP β was a sole carbohydrate model compound, or when a pair of MGP β and another carbohydrate model compound was treated. Figure 7 indicates how the degradation of MGP β was affected by the co-existence of another carbohydrate compound. The degradation of MGP β was suppressed by the co-existence of MGP α , MAP, or MGaP but enhanced by that of MMP. The suppression is understandable, because these co-existing carbohydrate model compounds compete with MGP β in the reaction with AOS. It is suggested that the degradation of MMP is efficiently accompanied by the generation of some AOS that attack MGP β . Figure 8 is created similar to Fig. 7, and shows the degradation of MGP α , MMP, MAP, or MGaP in the TMPH system, when each of them was a sole carbohydrate model compound or a pair of MGP β and each of them was treated. It is similarly seen from Fig. 8 how the degradation of each compound was affected by the

co-existence of $MGP\beta$. The co-existence of $MGP\beta$ did not largely change the degradation of $MGP\alpha$, suppressed that of MAP or MGaP, and enhanced that of MMP, although the suppression is understandable as described above. The obtained results seem to suggest that the generation of AOS is relatively efficient when MMP is present in the system and that the profile of AOS generated in the system is dependent not only on the type of phenolic compound [8–10], the generator of AOS, but also on that of the carbohydrate model compound.

Figure 9 illustrates the quantitative correlation between the degradation of a carbohydrate model compound and

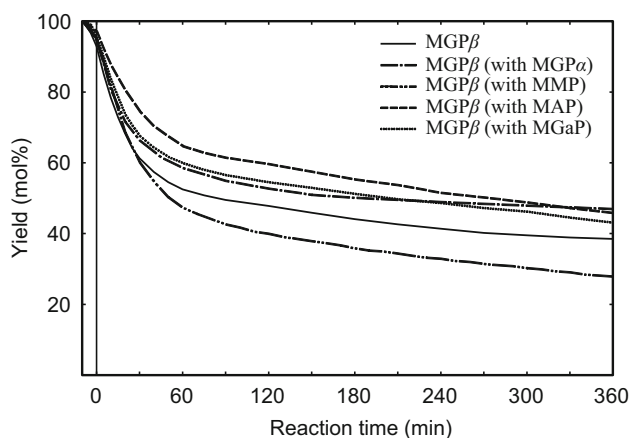


Fig. 7 Change in the yield of $MGP\beta$ when $MGP\beta$ as a sole carbohydrate model compound or a pair of $MGP\beta$ and another carbohydrate model compound was subjected to the TMPH system

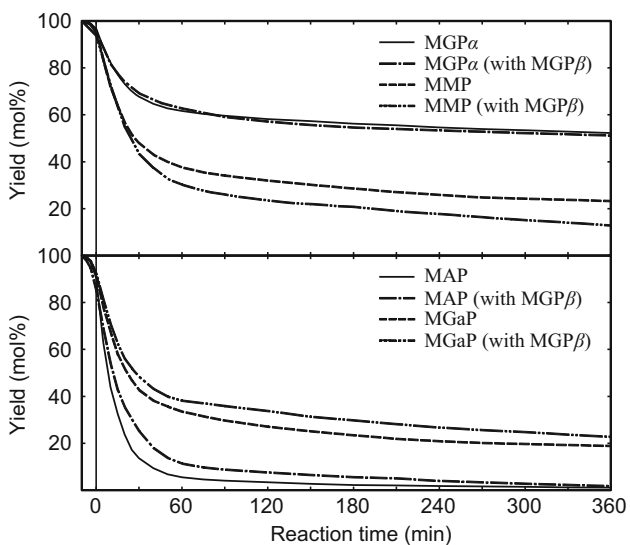


Fig. 8 Change in the yields of $MGP\alpha$ (upper), MMP (upper), MAP (lower), and MGaP (lower) when each of them as a sole carbohydrate model compound or a pair of $MGP\beta$ and each of them was subjected to the TMPH system

that of a phenolic compound, TMPH or Valc. Several phenomena can be recognized from Fig. 9. The difference in degradation between $MGP\beta$ and the other carbohydrate model compound seems to be smaller in the TMPH than in the Valc system for the reaction of any pair, when TMPH or Valc still exists. However, the degradation of any carbohydrate model compound seems to be greater in the TMPH than in the Valc system after TMPH or Valc disappears. The degradation of the carbohydrate model compound is clearly greater in the Valc than in the TMPH system only for the reaction of a pair of $MGP\beta$ and MAP, when TMPH or Valc still exists. On the other hand, the degradation is similar in both systems in the reaction of the other three pairs, when TMPH or Valc still exists. These phenomena indicate that the profile of AOS is not exactly the same in both systems both before and after TMPH or Valc disappears from the system. The degradation products of TMPH may generate some AOS that initiate chain-type reactions more efficiently than those from Valc. MAP as well as co-existing $MGP\beta$ is sensitive to the difference in the profile of AOS between the TMPH and Valc systems.

Conclusions

The stereo-configurational difference of the carbohydrate model compound affects the reaction with AOS differently depending on the location of the difference. The degrees of

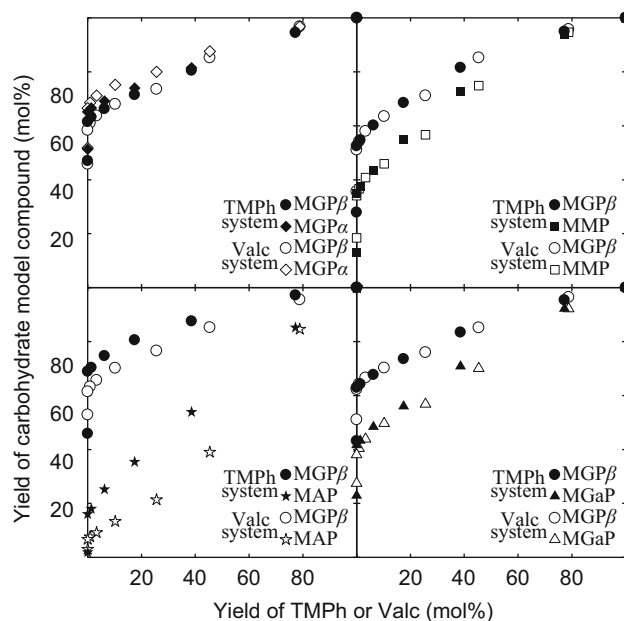


Fig. 9 Correlation between the residual yields of carbohydrate model and phenolic compounds when a pair of $MGP\beta$ and $MGP\alpha$ (upper left), of $MGP\beta$ and MMP (upper right), of $MGP\beta$ and MAP (lower left), or of $MGP\beta$ and MGaP (lower right) was subjected to the TMPH (filled marks) or Valc (open marks) system

degradation of the employed carbohydrate model compounds were in the order of $MGP\alpha < MGP\beta < MMP < MGaP < MAP$ in all systems, and the degradation of MAP was especially great. We suggest that the orientation of their three secondary hydroxy groups is a determining factor in their degradability. In the reaction of a pair of $MGP\beta$ and another carbohydrate model compound, only the co-presence of MMP enhanced the degradation of $MGP\beta$ and the co-presence of $MGP\beta$ enhanced the degradation of MMP, although as expected co-existence of the other carbohydrate model compounds mostly suppressed the degradation of $MGP\beta$ and co-existing $MGP\beta$ suppressed the degradation of other co-existing carbohydrate model compounds. These results suggest that the profile of AOS in the system is dependent not only on the type of phenolic compound, the generator of AOS, but also on that of carbohydrate model compound. MAP as well as co-existing $MGP\beta$ is sensitive to the difference in the profile of AOS between the TPh and Valc systems.

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