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Further evidence for the gelation ability–structure correlation in sugar-based gelators

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Abstract

Eight methyl glycosides of 4,6-*O*-benzylidene derivatives of the monosaccharides D-glucose, D-mannose, D-allose and D-altrose were synthesized to systematically study the effect of small configurational changes on the ability to gelate organic solvents. Among the β anomers, only the D-mannose glycoside exhibits a strong gelation ability, whereas in the α-series the D-glucose and D-mannose derivatives act as versatile gelators. Also, as a general rule we found that the β anomers possess a higher ability to gelate solvents than the α anomers. The gelation properties are discussed on the basis of SAXS, FTIR, differential scanning calorimetric (DSC) measurements and scanning electron microscopy (SEM) observations. The temperature-dependent SAXS measurements were carried out to elucidate the sol–gel transition temperature. The present study emphasizes that the saccharide family provides, not only valuable information of the structural requirements for the design of new gelators, but also for molecular assembly systems in general.

Keywords: Carbohydrates; Gels; Hydrogen bonds; Sol–gel process; Supramolecular chemistry

1. Introduction

The development of new gelators for organic solvents has recently received much attention. They not only gelate various organic solvents, but also create novel networks with fibrous superstructures that can be characterized by SEM pictures of xerogels.[1–12] According to their driving forces for molecular aggregation, gelators can be classified into two categories: hydrogen-bond-based gelators and nonhydrogen-bond-based gelators. Aliphatic amide derivatives[1–4] are typical examples of the former group, whereas cholesterol derivatives[6–9] are the main representatives of the latter group. Saccharide-containing gelators have also been reported to form a hydrogen-bond-based gel network as well, but their examples in literature are very limited.[8,13–16] In recent studies some methyl glycosides of 4,6-*O*-benzylidene monosaccharides have been investigated with regard to their ability to gelate organic solvents. However, the exact relationship between the structure and the gelation potential has remained unknown. In this pa-

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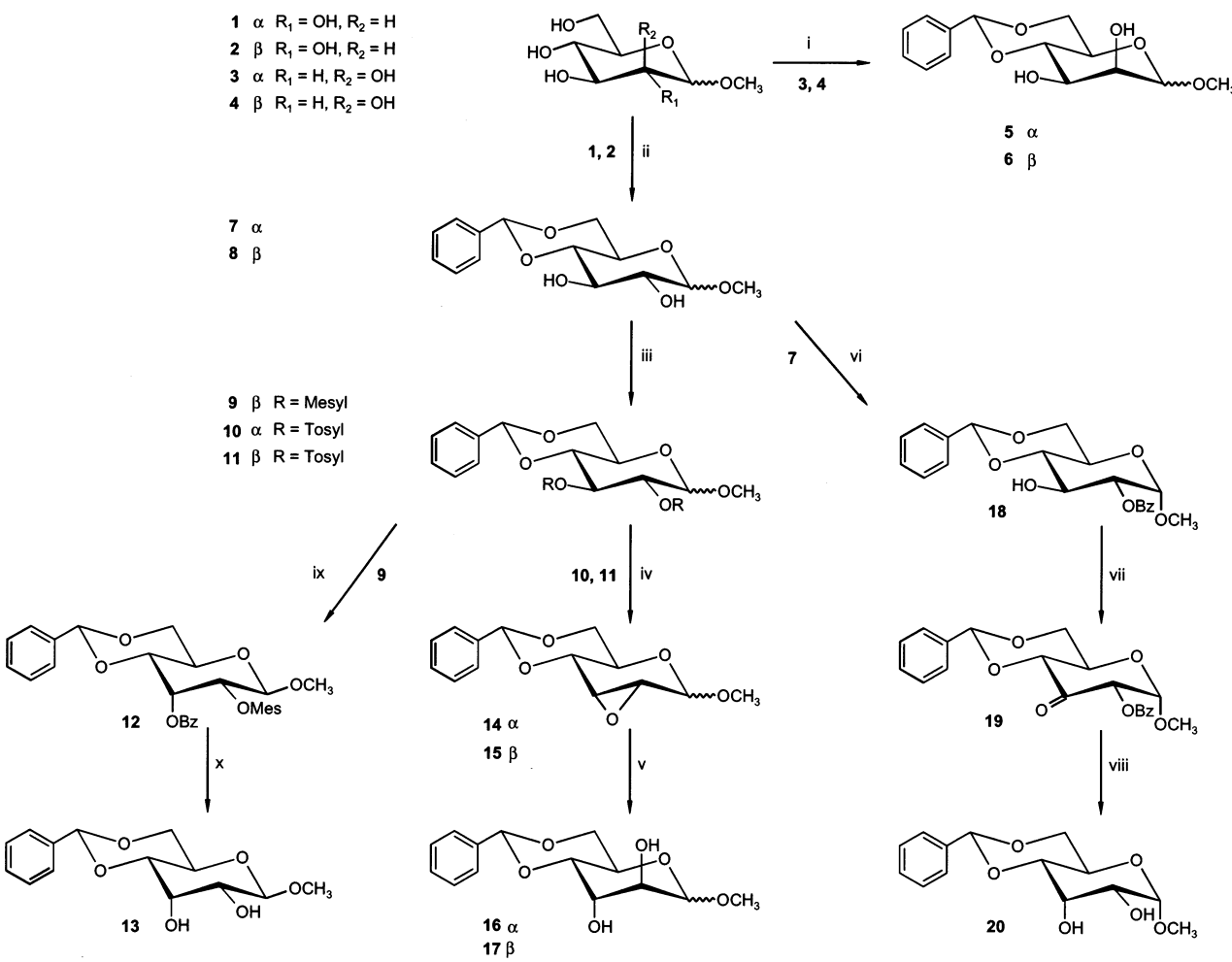
per, we report the synthesis and detailed examination of the α and β isomers of gluco, manno, allo and altropyranoside, from which further evidence for the correlation between the absolute configuration and the gelation ability has been obtained.

2. Results and discussion

Synthesis.—The syntheses of the eight sugar compounds tested are outlined in Scheme 1. Treatment of methyl α,β-D-mannopyranoside (**3**, **4**) with α,α-dimethoxytoluene under slightly acidic conditions[17] yielded the 4,6-*O*-benzylidenated derivatives **5** and **6** as the main products. The acetalation of the C-4 and C-6 hydroxyl groups in methyl α-(**1**) and β-D-glucopyranoside (**2**) was carried out with $ZnCl_2$ and benzaldehyde.[16] Methyl 4,6-*O*-benzylidene-α and β-D-glucopyranoside (**7** and **8**) served not only as compounds for gelation experiments but also as important key intermediates for synthesis of the allo and altro monosaccharides. Compound **8** was converted according to literature[18] into the 2,3-di-*O*-(methylsulfonyl) derivative **9** and then treated with sodium benzoate in *N*,*N*-dimethylformamide to replace the sulfoxy-group at C-3, with inversion of the configuration, to give methyl 3-*O*-benzoyl-4,6-*O* - benzylidene - 2 - *O* - (methylsulfonyl) - β - D-allopyranoside (**12**) in 61% yield. Treatment of **12** with lithium aluminum hydride in 1,4-dioxane simultaneously removed the methylsulfonyloxy group, with splitting of the O–S



Scheme 1. (i) $PhCH(OCH_3)_2$, PPTS, DMF, 5–6.5 h at 80 °C. (ii) PhCHO, $ZnCl_2$, stirring overnight at rt. (iii) TsCl, pyridine, 4 days at rt (**7**, **8**), MsCl, pyridine, 20 h at rt (**8**). (iv) CH_3ONa, $ClCH_2CH_2Cl$, 3 days refrigerator and then 2 days at rt. (v) KOH, H_2O, 2 days reflux. (vi) PhCOCl, imidazole, $CHCl_3$, 2 h reflux. (vii) DMSO, Ac_2O, 9 h at rt. (viii) $NaBH_4$, DMF, MeOH, 45 min at rt and then reflux for 10 min. (ix) $PhCO_2Na$, DMF, reflux. (x) $LiAlH_4$, 1,4-dioxane, 80 °C for 18 h.

bond and the benzoyl group, to afford methyl 4,6-*O*-benzylidene-β-D-allopyranoside (**13**)[19] in 69% yield. The corresponding α-allo anomer (**20**) was prepared by selective benzoylation of the C-2 hydroxyl group in **7**, followed by oxidation of the C-3 position with dimethyl sulfoxide and acetic anhydride to afford methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose (**19**)[20] in 60% yield. Finally, methyl 4,6-*O*-benzylidene-α-D-allopyranoside (**20**) was obtained by reduction of **19** with sodium borohydride in MeOH–*N*,*N*-dimethylformamide. The yield of 72% was found to be better than that reported in literature (55%).[21]

Tosylation of methyl 4,6-*O*-benzylidene-α and β-D-glucopyranoside (**7** and **8**) to the 2,3-di-*O*-tosyl derivatives **10** and **11**, and their treatment with sodium methylate in 1,2-dichloroethane gave the corresponding methyl 2,3-anhydro-4,6-*O*-benzylidene-α- and β-D-allopyranosides (**14**[22] and **15**[23]) in quantitative yields. Hydrolysis with alkali[22,24] induced the ring opening with inversion at C-2 and the formation of a mixture of methyl 4,6-*O*-benzylidene-α and β-D-glucopyranoside (**7** and **8**) and methyl 4,6-*O*-benzylidene-α and β-D-altropyranoside (**16** and **17**), with the latter as the principal product. The altro:gluco ratio was estimated via ^{1}H NMR spectroscopy for the α anomer to be 85:15 and 70:30 for the β anomer, respectively. All compounds were identified by spectroscopic methods and compared with published data. HPLC analysis ($\lambda = 210$ nm) confirmed that the purity of the target compounds used for the gelation test was higher than 98%.

Gelation test for various solvents.—The gelation test was carried out as follows: the gelator (2.4–3.5 mg) was mixed in a closed-capped test tube with the appropriate amount of solvent (80–110 μL) to result in a concentration of 3 wt.%, and the mixture was heated until the solid was dissolved. By this procedure the solvent bp became higher than under standard atmospheric pressure. The sample vial was cooled in air to 25 °C, left for 1 h at this temperature, and then turned upside down. When the gelator formed a clear or slightly opaque gel by immobilizing the solvent at this stage, it was denoted by a 'G' in Table 1. Some solutions gelled at a gelator concentration below 1 wt.%. These results are marked with an '*'. As with previous studies,[16a] the solvents tested were classified into two groups: Group I solvents are gelated by some compounds, whereas Group II solvents mainly result in solutions. In contrast, this time only carefully dried solvents were used to exclude the possible influence of water on the gelation results. Furthermore, we introduced the self-supporting precipitate (P_S) as a new classification additional to gel (G) and precipitation (P). In this stage the monosaccharide establishes a turbid self-supporting structure in the solvent consistent with fibrous aggregates immobilizing, similar to the gel, the complete volume of the solvent. However, this aggregation type does not completely fulfill the requirements of a true physical gel. The transition from 'gel phase' to a solution is not reversible since slow cooling causes crystallization, and mechanical disruption (shaking) causes a visible separation into a solid and a liquid phase. When the compound aggregated only parts of the solvent in a similar manner to those of P_S, we denoted this as a partial self-supporting precipitation (P_{PS}). Due to these changes we reinvestigated the previously tested[16a] compounds **5**, **7** and **8** and found that some of the reported gels (G) have to be rejudged as P_S or P_{PS} (**5**: entry 4; **7**: entry 1, 3 and 5; **8**: entries 11 and 13), whereas in some cases P changes into P_S (**5**: entry 6; **7**: entries 2, 4, 18 and 20; **8**: entries 1–10, 12, 15, 16, 18, 21–25, 27 and 30–34). On the other hand, we observed the gel-formation instead of precipitation for **7** in tetraethoxysilane (entry 19).

From comparison of all compounds listed in Table 1, several conclusions can be drawn: Firstly, among α-monosaccharides **5**, **7**, **16** and **20** only the gluco (**7**) and the manno (**5**) diastereomers act as gelators. Both gelate aromatic solvents like toluene, *p*-xylene and diphenyl ether. Additionally, the α-manno diastereomer (**5**) can also gelate apolar hydrocarbons (*n*-hexane, *n*-heptane, *n*-octane, methylcyclohexane), carbon disulfide, triethylsilane and water, whereas the α-gluco compound (**7**) gelates benzene and tetraethoxysilane. In apolar hydrocarbon solvents (*n*-hexane to methylcyclohexane) triethylsilane and tetraethoxysilane **7** forms a gel-like pre-

Table 1
Organic solvents tested for gelation by **5**, **6**, **7**, **8**, **13**, **16**, **17** and **20** [a]

	Organic solvent	**5**	**7**	**16**	**20**	**6**	**8**	**13**	**17**
Group I									
1	*n*-hexane [b]	G*	P_S^*	I*	P*	G*	P_S^*	P_S^*	P*
2	*n*-heptane [b]	G*	P_S^*	I*	P*	G*	P_S^*	P_S^*	P*
3	*n*-octane [b]	G*	P_S^*	P*	P	G*	P_S^*	P_S^*	P*
4	cyclohexane [b]	P_S^*	P_S^*	P*	P	G*	P_S^*	P_S^*	P_S^*
5	methylcyclohexane [b]	G*	P_S^*	P_{PS}^*	P	G*	P_S^*	P_S^*	P*
6	benzene [b]	P_S^*	G	P_{PS}	P_{PS}	G*	P_S^*	P_S	P_{PS}
7	toluene [b]	G*	G*	P_{PS}	P_{PS}	G*	P_S^*	P_S^*	P_S
8	*p*-xylene [b]	G*	G*	P_{PS}	P_{PS}	G*	P_S^*	P_S^*	P_S
9	nitrobenzene [b]	S	S	S	S	S	P_S	S	S
10	carbon tetrachloride [b]	P	G*	P*	P	G*	P_S^*	P_S^*	P
11	carbon disulfide [c]	G*	P*	P*	P*	G*	P_{PS}^*	P_S^*	P_S
12	diethyl ether [b]	S*	S*	P*	P	S*	P_S^*	P*	P*
13	diphenyl ether [b]	G	G	P_{PS}	P_{PS}	G	P_S^*	P_S	P_{PS}
14	ethyl formate [b]	S	S	S	S	S	P*	S	S
15	methyl acetate [b]	S	S	S	S	S	P_S	S	P
16	*n*-octanol [b]	S	S	S	S	P	P_S	P_S	P
17	triethylamine	S	S*	S*	S*	S	P*	S	P
18	triethylsilane	G*	P_S^*	S*	P	G*	P_S^*	P_S^*	P*
19	tetraethoxysilane	S	G*	P_{PS}^*	P	P	P*	P	P
20	water	G	P_S	S	S	S	P*	P_S	P
Group II									
21	1,2-dichloroethane	S	S	S	S	S	P_S^*	S	P
22	dichloromethane [b]	S	S	S	S	S	P_S	S	P
23	chloroform	S	S	S	S	S	P_S	S	S
24	ethyl acetate [b]	S	S	P	S	S	P_S	P	P
25	ethyl malonate [b]	S	S	S	S	S	P_S	S	S
26	acetone [b]	S	S	S	S	S	P	S	S
27	methyl ethyl ketone [b]	S	S	S	S	S	P_S	P	P
28	acetonitrile [b]	S	S	S	S	S	P	P	P
29	ethanol [b]	S	S	S	S	P	P	P	S
30	*n*-propanol [b]	S	P	S	S	P	P_S	P	S
31	*n*-butanol [b]	S	P	S	S	P_S	P_S	P_S	S
32	hexanoic acid	S	S	S	S	P	P_S	P_S	P
33	acetic anhydride	S	S	S	S	S	P_S	S	S
34	glycerol	S	S	S	S	S	P_S	S	S

[a] 3.0 wt./vol% unless specified otherwise: *, 1.0 wt./vol%; G, gel; P_S, self-supporting precipitate; P_{PS}, partial self-supporting precipitate; P, precipitation; S, solution; I, insoluble.
[b] Dried over 4 Å molecular sieves.
[c] Dried over anhydr $MgSO_4$.

cipitation that is denoted by 'P_S'. In contrast, the α-allo (**13**) and α-altropyranoside (**16**) tend to be insoluble or precipitate in the Group I solvents. In some cases theses saccharides partially immobilize the solvents by the formation of the self-supporting precipitates denoted as 'P_{PS}'. In accordance with previous studies, all α compounds form mainly solutions in Group II solvents.

On the other hand, among the β isomers only the manno diastereomer **6** can be considered as a gelator. It gelates a wide range of solvents such as apolar hydrocarbons and aromatic solvents (entries 1–8 and 13), carbon tetrachloride, carbon disulfide and triethylsilane mainly at 1 wt.% concentration. In contrast, the β-gluco and allopyranosides (**8** and **13**) tend to form mainly self-supporting precipitates as denoted by the numerous 'P_S' marks. Similarly, the β-altropyranoside (**17**) exhibits a low solubility in the major part of the solvents tested reflected by the 'P' and 'P_S' marks.

At first a general conclusion that one can draw from Table 1 is that the absolute conformation of the monosaccharides strongly influences the gelation ability. Among the α-monosaccharides, the gluco and the manno diastereomer can be considered as gelators, whereas among the β anomers only methyl 4,6-*O*-benzylidene-β-D-mannopyranoside (**6**) possesses the ability to gelate solvents. A more detailed picture is given by the investigation of the concentration dependence of the sol–gel transition temperatures (T_{gel}).

Concentration dependence.—In Fig. 1 the sol–gel phase-transition temperatures (T_{gel}) of **5**, **6** and **7** in *p*-xylene and diphenyl ether are plotted against the gelator concentration in order to compare their gelation properties. The use of dried solvents caused for compound **6** no change in T_{gel} compared to the previously obtained data.[16a] For the same concentration the T_{gel} values always appear in the order of **6** > **7** > **5**. However, the T_{gel} for **7** were only evaluated in between 0.5 and 1.0 wt.%. At higher concentrations a self-supporting precipitation (P_S) is formed, and below 0.5 wt.% no gelation occurs. Furthermore, the gel of **7** formed in *p*-xylene is less stable than that of the manno compounds. Within a few days crystals are formed, whereas the manno gels are stable for weeks. Together with the results from Table 1, these findings suggest the order for the gelation ability to be β-manno > α-manno > α-gluco. Although the T_{gel} for **7** in *p*-xylene between 0.5 and 1.0 wt.% and in diphenyl ether is higher than that for **5**, the smaller variety of other solvents gelated by α-gluco (**7**) implies that compound is inferior to α-manno (**5**).

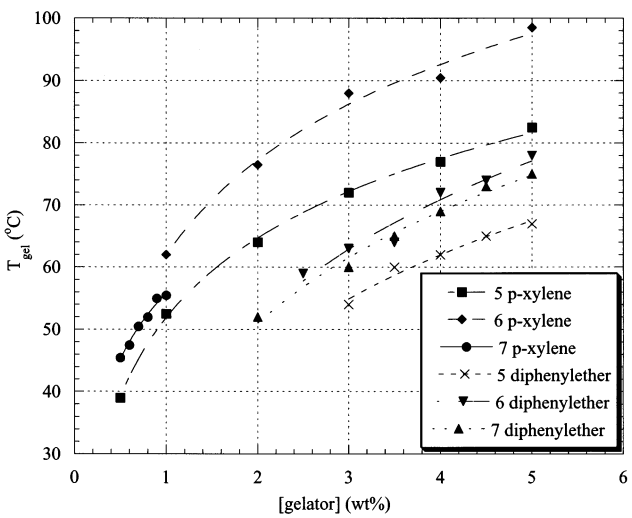


Fig. 1. Plots of T_{gel} against gelator concentration in *p*-xylene and diphenyl ether.

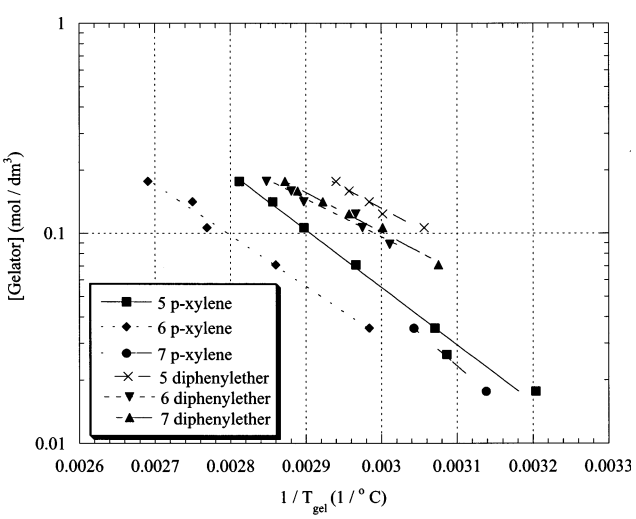


Fig. 2. Plots of log[gelator] (gelator concentration in mol/dm^3) against T_{gel}^{-1} in *p*-xylene and diphenyl ether.

Eq. (1), which is derived from Schrader's relation, allows the calculation of ΔH for the dissolution of solid compounds in organic solvents.[7] ΔH can be determined from the slope of a plot of log[gelator] (with the gelator concentration given in mol/dm^3) against T_{gel}^{-1}. Because these ΔH values are comparable or slightly larger than the latent heat of melting (ΔH_m) determined from DSC measurements at the melting point of the solid, it has been assumed that this ΔH_{gel} value reflects the heat released at the sol–gel phase-transition temperature.[7] Recent studies[7,16,25] proposed, therefore, a low degree of solvation for the fiber structures formed by the gelator molecules in the organic solvent. Fig. 2 shows the straight lines of the plots of log[gelator] against T_{gel}^{-1} with γ (correlation coefficients) > 0.98. The ΔH_{gel} values are summarized, together with the ΔH_m values as obtained by DSC measurements at the melting point in Table 2.

$$\log[\text{gelator}] = -\frac{\Delta H}{2.303R} \times \frac{1}{T_{gel}} + \text{constant} \quad (1)$$

In general, the ΔH_{gel} values in *p*-xylene are higher than those in diphenyl ether. This corresponds with the higher concentrations (> 2

Table 2
ΔH_{gel} obtained from [gelator] vs. T_{gel} plots in *p*-xylene and diphenyl ether and ΔH_m at the melting point obtained from DSC measurements [a]

		ΔH_{gel} (kJ/mol)		ΔH_m (DSC) (kJ/mol)
		p-xylene	Diphenyl ether	
α-Series	**7** (gluco)	56.8	36.2	16.0
	5 (manno)	52.3	37.7	10.1
	20 (allo)			30.9
	16 (altro)			23.1
β-Series	**8** (gluco)			27.2
	6 (manno)	46.5	34.8	18.2
	13 (allo)			28.0
	17 (altro)			25.4

[a] All correlation coefficients are >0.98.

wt.%) required for gel-formation in this solvent if one attributes a small ΔH_{gel} value to the affinity (or partial dissolution) of the gelator for the solvents molecules. Furthermore, diphenyl ether can act as a hydrogen-bond acceptor and weakens the network formation based on the intermolecular hydrogen-bonding interaction. For *p*-xylene ΔH_{gel} decreases in the order $\mathbf{7} > \mathbf{5} > \mathbf{6}$, whereas in diphenyl ether the order was estimated to be $\mathbf{5} > \mathbf{7} > \mathbf{6}$. In general, the β-manno derivative (**6**) has the highest affinity to the solvent molecules.

As expected for all monosaccharides, the ΔH_{gel} values are larger than the corresponding ΔH_m values, since ΔH_{gel} values are associated with solvation, whereas ΔH_m values are not. Interestingly, a comparison of ΔH_m values for all compounds reveals that the monosaccharides acting as gelators possess, in general, smaller values (16.0, 10.1, 18.7 kJ/mol) than the non-gelators (20–30 kJ/mol). Therefore, the less cohesive nature of the monosaccharides seems to be beneficial for their ability to gelate solvents.

FTIR spectroscopy.—The evidence that 4,6-*O*-benzylidene monosaccharides form a hydrogen-bond-based gel-network has been investigated in detail by FTIR and temperature-dependent ^{1}H NMR spectroscopy.[16a] Therefore, in this paper only a brief confirmation by FTIR spectroscopy is given. Due to intermolecular and intramolecular hydrogen-bonding interactions, no ν_{OH} peak for a free OH group (around 3600 cm^{-1}) could be detected for the solid samples (KBr) of all the monosaccharides. In the gel-state, all signals are more broadened, and the ν_{OH} for the OH groups appear in the range of 3047–3483 cm^{-1} [**5**: 3047 (vs), **6**: 3262 (s), 3467 (s), 3566 (s), **7**: 3047 (vs); (all in carbon tetrachloride, 1 wt.%)] and can therefore be assigned to the intermolecular hydrogen bonds in the gel network. For only the β-manno derivative (**6**) a sharp peak appears at 3566 cm^{-1}, which indicates the presence of nonhydrogen-bonded OH groups.

Synchrotron small angle X-ray scattering.—Synchrotron small-angle X-ray scattering (SAXS) is a powerful method to explore supramolecular structure. Since the synchrotron X-ray is almost 10^6 times stronger than conventional X-rays, it has great advantage for diluted systems such as organogels. Terech et al.[26–28] analyzed SAXS from different non-sugar-based organogelators. We measured SAXS for the first time from sugar-based organogelators and investigated from the β-series the gluco, manno and allo diastereomers and α-mannopyranoside (**5**) at 1 wt.% in *p*-xylene. The scattering patters obtained are clearly different (Fig. 3). The manno diastereomer of the β-series (**6**) shows at room temperature a broad peak at $q = 0.018$ that is probably due to the supramolecular structure of the gel and a second peak at $q = 0.014$ $Å^{-1}$. Also the α-mannopyranoside (**5**) exhibits similar broad peaks at $q = 0.04$ and 0.09 $Å^{-1}$ from which the first can be assigned to the gel structure as well. SAXS measurements of the self-supporting precipitation (P_S) from β-gluco- and allopyranoside (**7**, **13**) gave typical scattering curves that are obtained from polydisperse systems by the superposition of the component curves. This supports the assumption that P_S contains particles of identical shape but too different in size to form a gel. An attempt to obtain scattering data from the α-glucosaccharide (**7**) 1 wt.% in *p*-xylene failed, probably due to the small contrast to give scattering.

In order to investigate which peaks are related to the gel structure, a temperature-dependent measurement was carried out with **6** in *p*-xylene (1.5 wt.%). Fig. 4 shows the scattering profiles obtained at 50, 60, 65, 70 and 80 °C. At 50 °C the curve contains two broad peaks at $q = 0.018$ and 0.11 $Å^{-1}$. With increasing temperature (60 °C) the position of the peaks remains unchanged; however, the intensity of the peak at $q = 0.018$ $Å^{-1}$ decreases about 50% and it disappears completely at 70 °C. Because the sol–gel transition temperature (T_{gel}) of this system was estimated by the oil-bath method to be 70 °C, this result supports the assumption that the first peak can be assigned to the supramolecular structure of the gel. A similar experiment was carried out with **5** in *p*-xylene (1.5 wt.%), and the peak at $q = 0.04$ $Å^{-1}$ disappeared as expected between 60 and 65 °C ($T_{gel} = 60$ °C). Furthermore, the clearer scattering pattern of **6** compared to **5** is probably due to a more homogenous particle size in the gel, which corresponds with the higher T_{gel}. Therefore, the SAXS measurements support the conclusions that **5** is inferior to **6** derived by the T_{gel} measurements. The problem of improving the scattering quality is currently under investigation to obtain more intense peaks that allow a fit to a model for the molecular packing in the gel state.

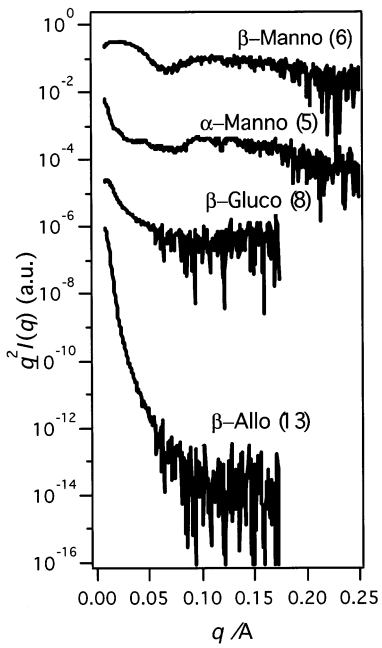


Fig. 3. Scattering profile for **5**, **6**, **7** and **13** (1 wt.% in *p*-xylene) at room temperature.

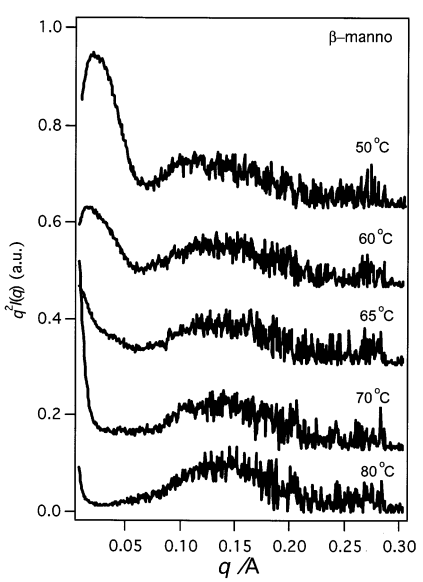


Fig. 4. Temperature dependence of the SAXS profiles for **6** (1.5 wt.% in *p*-xylene).

SEM observation of xerogels.—To obtain visual insights into the aggregation mode, dry samples of organic gel fibers for SEM studies have been prepared.[29] It is clear that gelators form a three-dimensional fiber network. Fig. 5 shows typical pictures obtained from xerogel of **6** in carbon disulfide and the self-supporting precipitates (P_S) of **8**, **13**, and **17** in *p*-xylene and carbon tetrachloride. As expected, the gelator **6** forms a three-dimensional network with puckered fibrils (200–500 nm diameter) that are connected with junction nodes. Probably a disorder in aggregation is the origin of these knots. We expected that the hydrogen-bonding interactions among chiral saccharide moieties might create a helical fiber structure, but such a periodic, regular structure was not found in these SEM pictures. Therefore, the absolute configuration is not reflected in the fiber shape. In contrast, the self-supporting precipitates show linear fibers with lengths over 30 μm and diameters around 5 μm. In none of these cases could junction points be observed. These results show that compounds possessing the ability to form a fiber structure do not necessarily act as good gelators.

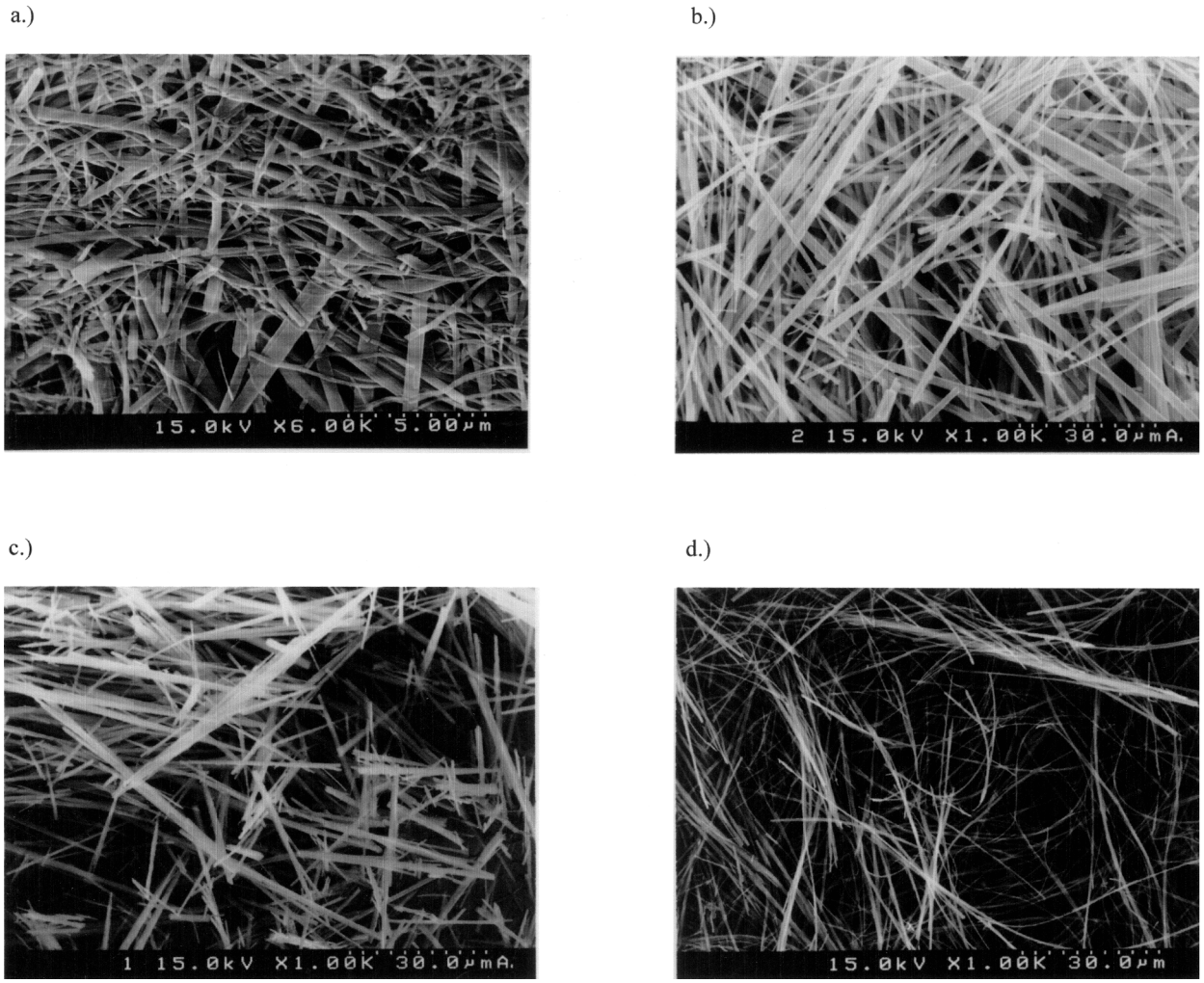


Fig. 5. SEM pictures of **6**, **8**, **13** and **17**. (a) **6** prepared from carbon disulfide [1% (wt./vol)]; (b) **8** prepared from carbon tetrachloride [1% (wt./vol)]; (c) **17** prepared from *p*-xylene [3% (wt./vol)]; (d) **13** prepared from *p*-xylene [1% (wt./vol)].

3. Conclusions

The present study has demonstrated that among the methyl glycosides of 4,6-*O*-benzylidene monosaccharides only gluco and manno in the α-series and methyl 4,6-*O*-benzylidene-β-D-mannopyranoside (**6**) act as efficient hydrogen-bond-based gelators. Judging from the T_{gel} and the variety of solvents gelated, the gelation capability for organic solvents decreases in the order of **6** > **5** > **7**. The comparison of both mannopyranosides confirms the conclusion derived from a previous study of D-galactose derivatives[16a] that the β anomer is more efficient than the α anomer. In summary, among ten investigated 4,6-*O*-benzylidene monosaccharides, only D-mannose, D-galactose derivatives and methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**7**) serve as gelators. Partly these differences can be explained by the mode of action as to these molecules gelate organic solvents. Since they form a one-dimensional hydrogen-bonding array under participation of both hydroxyl groups,[30] methyl 4,6-*O*-benzylidene-α-D-altropyranoside (**16**) and methyl 4,6-*O*-benzylidene-α-D-allopyranoside (**20**) cannot serve as efficient gelators because of the possible strong intramolecular 3-OH–1-OMe interaction between both axial orientated groups.[31] For the efficient formation of a gel, the hydrogen-bonding network to both hydroxyl groups should be orientated so that they can form one-dimensional intermolecular hydrogen bonds.

In addition, the gelation process depends on the gelator's ability to assemble into fiber-like aggregates. Although the β-series shows a

strong ability for fiber structure formation indicated by the SEM pictures, **8**, **13**, and **17** do not meet the requirements to gelate solvents. Due to the lack of junction nodes and the enhanced fiber thickness, these compounds are not able to form a three-dimensional fiber network. Based on the ΔH_m values obtained from DSC, these compounds must be considered as too cohesive to act as gelators. Consequently, they form instead of gels self-supporting precipitates. From this point of view α-gluco occupies an intermediate position because it forms Ps as well as gels. Therefore, the optimal requirements to be a gelator are fulfilled only by the 4,6-*O*-benzylidene derivatives of D-mannose and D-galactose.

The foregoing findings must be useful for the discovery and the design of new gelators. We believe that the saccharide library provided by nature can be applied further, in particular to the design of molecular assemblies, such as macrocyles, DNA mimics, monolayers, bilayer membranes and liquid crystals.

4. Experimental

General.—Compounds **9**,[18] **10**,[22] **11**,[23] **12**,[19] **14**,[22] **15**,[23] **18**,[20] and **19**[20] were prepared according to known literature methods. All compounds gave ^{1}H NMR spectra and mp's that correlated with those reported. New compounds were characterized by NMR, UV, IR and MS spectroscopy and elemental analysis. The purity of all target compounds **5**,[17] **6**, **7**,[16] **8**,[16] **13**,[19] **16**,[22] **17**,[24] and **20**[21] was confirmed by HPLC analysis.

Gel–sol transition temperatures.—The test tube containing the gel was immersed inversely in a thermostated oil bath. The temperature was raised at a rate of 2 °C/min. Here, the T_{gel} was defined as the temperature at which the gel turned into the sol-phase.

SEM observations.—A Hitachi S-900S scanning electron microscope was used for taking the SEM pictures. The gel was prepared in a sample tube and frozen in liquid N_2. The frozen specimen was evaporated by a vacuum pump for 10–15 h. The dry sample obtained was shielded with platin. The accelerating voltage of SEM was 5 kV and the emission current was 10 μA.

Apparatus for spectral measurements.—^{1}H and ^{13}C NMR spectra were measured with a Bruker ARX 300 instrument. Chemical shifts are reported downfield from the internal standard, Me_4Si. Spin–spin coupling is reported in Hz. For ^{13}C NMR data, DEPT assignments are indicated as follows: +, positive; −, negative; *, no signal. UV spectra were obtained using a JASCO V-570 spectrometer. IR spectra were recorded in KBr pills and NaCl cells (0.5 mm) with a Shimazu FTIR 8100 spectrometer. A Hitachi M-2500 spectrometer was used recording the mass spectra. The SIMS measurements were carried out in a glycerol or 3-nitrobenzylalcohol (NBA) matrix with xenon as a primary ion.

HPLC analysis.—HPLC analysis was carried out with a Waters 600 apparatus with a Waters 490E detector. A Millipore puresil column (5 μm, 120 Å C_{18} 0.6 × 150 mm) was used with a gradient of 30:70–70:30 MeCN–water in 20 min. Flow 1.5 mL/min. Detector: $\lambda = 210$ nm, aufs 1.0.

Synchrotron SAXS measurement.—The synchrotron SAXS measurement was carried out at the BL-15A SAXS station at the Photon Factory High Energy Research Organization in Japan. The SAXS intensity was collected as an accumulation of the scattered intensity during 100 s by use of a one-dimensional position sensitive detector with 20-cm length and 512 channels. Details of the optics and the instrumentation are described elsewhere.[32]

*Preparation of methyl 4,6-*O*-benzylidene-α-*D*-mannopyranoside* (**5**).—Compound **5** was prepared according to the published method.[17] R_f (1:1 EtOAc–hexane): 0.23. HPLC: T_R 10.87 min. mp 149.3–150.0 °C (lit. 141–143 °C[17]). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.73 (d, 1 H, $J_{3\text{-H, }3\text{-OH}}$ 2.1 Hz, 3-OH), 2.76 (d, 1 H, $J_{2\text{-H, }2\text{-OH}}$ 3.2 Hz, 2-OH), 3.39 (s, 3 H, OCH_3), 3.75–3.93 (m, 3 H, 2-H, 4-H, 6-H_A), 4.01–4.07 (m, 2 H, 3-H, 5-H), 4.28 (dd, 1 H, $J_{6\text{-H-B, }}$ 6-H-A 8.2, $J_{6\text{-H-B, }5\text{-H}}$ 2.8 Hz, 6-H_B), 4.74 (s, 1 H, 1-H), 5.56 (s, 1 H, 7-H), 7.36–7.39 (m, 3 H, Ar H), 7.47–7.50 (m, 2 H, Ar H). SIMS (6 keV, glycerol): m/z (%): 283 (79) $[M+H]^+$, 282 (4) $[M^+]$.

*Methyl 4,6-*O*-benzylidene-β-*D*-mannopyranoside* (**6**).—Methyl β-D-mannopyranoside isopropylate (**4**, 0.30 g, 1.18 mmol) and pyridinum *p*-toluenesulfonate (PPTS, 3.10 mg, 0.01 mmol) were placed in a flask and dissolved in 3 mL of dry DMF. The mixture was heated to 80 °C, and α,α-dimethoxytoluene (578 μL, 3.75 mmol) was added dropwise under a steady steam of dry N_2 to remove the liberated MeOH (6.5 h, 80 °C). The solvent was evaporated, and the residue was subjected to column chromatography (Wakogel C-300, 1:1 EtOAc–hexane) yielding 152.4 mg of a solid as a mixture of 4,6- and (*R*,*S*)-2,3-O-benzylidation products. This mixture was treated with *tert*-butyldiphenylchlorosilane (207 μL, 0.80 mmol) and *N*,*N*-dimethylaminopyridine (DMAP, 10.00 mg, 0.09 mmol) in 2.4 mL of dry pyridine for 4 h. The solvent was removed and the residue was subjected to column chromatography (Wakogel C-300, 2:1 EtOAc–hexane). Yield: 63 mg (0.22 mmol, 19%) of **6** as a colorless solid. R_f (2:1 EtOAc–hexane): 0.10. HPLC: T_R 7.99 min. mp 169.5–173.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.57 (d, 1 H, $J_{3\text{-H, }3\text{-OH}}$ 1.9 Hz, 3-OH), 2.66 (d, 1 H, $J_{2\text{-H, }2\text{-OH}}$ 6.4 Hz, 2-OH), 3.33–3.41 (m, 1 H, 5-H), 3.58 (s, 3 H, OCH_3), 3.80–3.93 (m, 3 H, 2-H, 4-H, 6-H_A), 4.11–4.12 (m, 1 H, 3-H), 4.35 (dd, 1 H, $J_{6\text{-H-B, }6\text{-H-A}}$ 10.5, $J_{6\text{-H-B, }5\text{-H}}$ 5.0 Hz, 6-H_B), 4.50 (d, 1 H, $J_{1\text{-H, }2\text{-H}}$ 1.1 Hz, 1-H), 5.56 (s, 1 H, 7-H), 7.36–7.38 (m, 3 H, Ar H), 7.48–7.51 (m, 2 H, Ar H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 66.5, 70.7, 70.8, 78.5 (+, C-2, C-3, C-4, C-5, O*C*H_3), 68.4 (−, C-6), 101.2, 102.0 (+, C-1, C-7), 126.2, 128.2, 129.1 (+, Ar C), 137.0 (*, Ar C). IR (KBr) ν_{max} (cm^{-1}): 696 (m), 723 (w), 760 (w), 787 (w), 980 (m), 991 (m), 1049 (s), 1103 (vs), 1172 (m), 1238 (m), 1385 (m), 1452 (m), 2883 (s), 3454 (vs), 3534 (vs). UV(MeOH) λ_{max} (log ε): 207.5 nm (3.87). SIMS (6 keV, glycerol): *m*/*z* (%): 283 (100) $[M+H]^+$, 282 (4) $[M^+]$. Anal. Calcd for $C_{14}H_{18}O_6$ (282.3): C, 59.56; H, 6.42. Found C, 59.59, H, 6.48.

*Preparation of methyl 4,6-*O*-benzylidene-α-*D*-glucopyranoside* (**7**).—Compound **7** was prepared according to the published method.[16] R_f (3:1 EtOAc–hexane): 0.17. HPLC: T_R 9.71 min. mp 164.6–166.4 °C (lit. 165.4–166.8 °C[16]). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.42 (s, 3 H, OCH_3), 3.46 (dd, 1 H, $J_{4\text{-H, }3\text{-H}}$ 9.2, $J_{4\text{-H, }5\text{-H}}$ 9.2 Hz, 4-H), 3.59 (dd, 1 H, $J_{2\text{-H, }}$ 1-H 3.9, $J_{2\text{-H, }3\text{-H}}$ 9.2 Hz, 2-H), 3.71 (dd, 1 H, $J_{6\text{-H-A, }6\text{-H-B}}$ 9.5, $J_{6\text{-H-A, }5\text{-H}}$ 9.5 Hz, 6-H_A), 3.71–3.79 (m, 1 H, 5-H), 3.90 (dd, 1 H, $J_{3\text{-H, }2\text{-H}}$ 9.2, $J_{3\text{-H, }4\text{-H}}$ 9.2 Hz, 3-H), 4.26 (dd, 1 H, $J_{6\text{-H-B, }6\text{-H-A}}$ 9.5, $J_{6\text{-H-B, }5\text{-H}}$ 3.7 Hz, 6-H_B), 4.75 (d, 1 H, $J_{1\text{-H, }}$ 2-H 3.9 Hz, 1-H), 5.50 (s, 1 H, 7-H), 7.33–7.37 (m, 3 H, Ar H), 7.46–7.49 (m, 2 H, Ar H). SIMS (6 keV, glycerol): *m*/*z* (%): 283 (21) $[M+H]^+$.

*Preparation of methyl 4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**8**).—Compound **8** was prepared according to the published method.[16] R_f (3:1 EtOAc–hexane): 0.31 HPLC: T_R 9.05 min. mp 207.3–208.6 °C (lit. 174–175 °C[16]). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.67, 2.83 (d, 1 H, *J* 2.5, *J* 2.4 Hz, 2-OH, 3-OH), 3.34–3.53 (m, 2 H, 2-H, 5-H), 3.52 (dd, 1 H, $J_{4\text{-H, }3\text{-H}}$ 9.0, $J_{4\text{-H, }5\text{-H}}$ 9.0 Hz, 4-H), 3.58 (s, 3 H, OCH_3), 3.79 (dd, 1 H, $J_{6\text{-H-A, }6\text{-H-B}}$ 10.5, $J_{6\text{-H-A, }5\text{-H}}$ 10.5 Hz, 6-H_A), 3.82 (ddd, 1 H, $J_{3\text{-H, }3\text{-OH}}$ 2.3, $J_{3\text{-H, }}$ 2-H 9.0, $J_{3\text{-H, }4\text{-H}}$ 9.0 Hz, 3-H), 4.33 (d, 1 H, $J_{1\text{-H, }2\text{-H}}$ 7.7 Hz, 1-H), 4.35 (dd, 1 H, $J_{6\text{-H-B, }6\text{-H-A}}$ 10.5, $J_{6\text{-H-B, }5\text{-H}}$ 9.2 Hz, 6-H_B), 5.54 (s, 1 H, 7-H), 7.36–7.38 (m, 3 H, Ar H), 7.48–7.51 (m, 2 H, Ar H). SIMS (6 keV, glycerol): *m*/*z* (%): 283 (13) $[M+H]^+$.

*Preparation of methyl 4,6-*O*-benzylidene-β-*D*-allopyranoside* (**13**).—Compound **13** was prepared according to the published method.[19] R_f (3:1 EtOAc–hexane): 0.23. HPLC: T_R 8.93 min. mp 171.5–172.5 °C (lit. 173–174 °C[19]). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.56 (bs, 1 H, 3-OH), 2.67 (d, 1 H, $J_{2\text{-OH, }2\text{-H}}$ 6.3 Hz, 2-OH), 3.47–3.53 (m, 1 H, 2-H), 3.57 (s, 3 H, 1-OCH_3), 3.58 (dd, 1 H, $J_{4\text{-H, }3\text{-H}}$ 2.5, $J_{4\text{-H, }5\text{-H}}$ 9.3 Hz, 4-H), 3.76 (dd, 1 H, $J_{6\text{-H-A, }6\text{-H-B}}$ 10.3, $J_{6\text{-H-A, }5\text{-H}}$ 10.3 Hz, 6-H_A), 3.95–4.04 (m, 1 H, 5-H), 4.37 (bs, 1 H, 3-H), 4.40 (dd, 1 H, $J_{6\text{-H-B, }}$ 6-H-A 10.4, $J_{6\text{-H-B, }5\text{-H}}$ 5.0 Hz, 6-H_B), 4.62 (d, $J_{1\text{-H, }2\text{-H}}$ 7.9 Hz, 1 H, 1-H), 5.57 (s, 1 H, 7-H), 7.35–7.39 (m, 3 H, Ar H), 7.46–7.51 (m, 2 H, Ar H). SIMS (6 keV, NBA): *m*/*z* (%): 283 (36) $[M+H]^+$, 282 (4) $[M^+]$.

*Preparation of methyl 4,6-*O*-benzylidene-α-*D*-altropyranoside* (**16**).—Compound **16** was prepared according to the published method.[22] R_f (2:1 EtOAc–hexane): 0.40. HPLC: T_R 9.31 min. mp 170.4–172.8 °C (lit. 169–170 °C[22]). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05, 2.88 (d,

1 H, *J* 5.9, *J* 6.7 Hz, 2-OH, 3-OH), 3.45 (s, 3 H, 1-OCH_3), 3.84 (dd, 1 H, $J_{6\text{-H-A, 6-H-B}}$ 10.1, $J_{6\text{-H-A, 5-H}}$ 10.1 Hz, 6-H_A), 3.98 (dd, 1 H, $J_{4\text{-H, 3-H}}$ 3.0, $J_{4\text{-OH, 5-H}}$ 9.1 Hz, 4-H), 4.03–4.06, 4.10–4.13 (m, 1 H, 2-H, 3-H), 4.17–4.26 (m, 1 H, 5-H), 4.35 (dd, 1 H, $J_{6\text{-H-B, 6-H-A}}$ 10.1, $J_{6\text{-H-B, 5-H}}$ 5.1 Hz, 6-H_B), 4.69 (s, 1 H, 1-H), 5.64 (s, 1 H, 7-H), 7.35–7.37 (m, 3 H, Ar H), 7.48–7.50 (m, 2 H, Ar H). SIMS (6 keV, glycerol): *m/z* (%): 283 (17) $[M+H]^+$, 282 (96) $[M^+]$.

*Preparation of methyl 4,6-*O*-benzylidene-β-*D*-altropyranoside* (**17**).—Compound **17** was prepared according to the published method.[24] R_f (2:1 EtOAc–hexane): 0.45. HPLC: T_R 8.91 min. mp 194.4–195.5 °C (lit. 188 °C[24]). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37, 2.51 (d, 1 H, *J* 1.4, *J* 1.8 Hz, 2-OH, 3-OH), 3.57 (s, 3 H, 1-OCH_3), 3.79–3.86 (m, 1 H, 5-H), 3.91–4.00 (m, 3 H, 2-H, 4-H, 6-H_A), 4.25–4.26 (m, 1 H, 3-H), 4.36 (dd, 1 H, $J_{6\text{-H-B, 6-H-A}}$ 10.3, $J_{6\text{-H-B, 5-H}}$ 2.9 Hz, 6-H_B), 4.79 (d, 1 H, $J_{1\text{-H, 2-H}}$ 1.1 Hz, 1-H), 5.61 (s, 1 H, 7-H), 7.26–7.29 (m, 3 H, Ar H), 7.41–7.50 (m, 2 H, Ar H). SIMS (6 keV, NBA): *m/z* (%): 283 (8) $[M+H]^+$, 282 (1) $[M^+]$.

*Preparation of methyl 4,6-*O*-benzylidene-α-*D*-allopyranoside* (**20**).—Compound **20** was prepared according to the published method.[21] R_f (2:1 EtOAc–hexane): 0.28. HPLC: T_R 8.89 min. mp 61.1–62.7 °C (lit. 63 °C[21]). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.59 (d, 1 H, $J_{3\text{-OH, 3-H}}$ 6.7 Hz, 3-OH), 2.87 (d, 1 H, $J_{2\text{-OH, 2-H}}$ 11.8 Hz, 2-OH), 3.49 (s, 3 H, 1-OCH_3), 3.57 (dd, 1 H, $J_{4\text{-H, 3-H}}$ 2.7, $J_{4\text{-OH, 5-H}}$ 9.7 Hz, 4-H), 3.68–3.75 (m, 1 H, 2-H), 3.76 (dd, 1 H, $J_{6\text{-H-A, 6-H-B}}$ 10.3, $J_{6\text{-H-A, 5-H}}$ 10.3 Hz, 6-H_A), 4.05–4.10 (m, 1 H, 5-H), 4.27–4.31 (m, 1 H, 3-H), 4.39 (dd, 1 H, $J_{6\text{-H-B, 6-H-A}}$ 10.3, $J_{6\text{-H-B, 5-H}}$ 5.1 Hz, 6-H_B), 4.78 (d, 1 H, $J_{1\text{-H, 2-H}}$ 4.1 Hz, 1-H), 5.59 (s, 1 H, 7-H), 7.36–7.39 (m, 3 H, Ar H), 7.48–7.50 (m, 2 H, Ar H). SIMS (6 keV, glycerol): *m/z* (%): 283 (32) $[M+H]^+$, 282 (100) $[M^+]$.

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