Exploitation of sugar ring flipping for a hinge-type tether assisting a [2 + 2] cycloaddition†

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Methyl 3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside (**2**) was exploited as a novel hinge-type tether for the [2 + 2] cycloaddition of cinnamate. The major ring conformation occupied by the 2,4-dicinnamate derivative of **2** was $^4C_1$, which extends two cinnamates along a diequatorial orientation. However, 3-*O*-deprotected dicinnamate **5**, when in a non-polar solvent, favours the $^1C_4$ conformation, which assists the approach of two cinnamates with the 1,3-diaxial scaffold. Photoirradiation of compound **5** at 313 nm in $CHCl_3$ afforded the intramolecular cycloaddition of cinnamates to give methyl β-, δ-, and ξ-truxinates in a 86 : 8 : 6 ratio after transesterification with methanol. The regio- and stereoselectivities are comparable to those reported by others for tethered cinnamates. The per-deuterated dicinnamate derivative of **5** facilitated the conformation analyses of the pyranoside rings by ^{1}H NMR, indicating that all the products of photoirradiation had $^1C_4$-fixed pyranosides. Excellent β-selectivity was achieved when *m*-bromocinnamate was subjected to hinge-tethered [2 + 2] cycloaddition.

Introduction

Tethered synthesis of organic compounds has been widely studied to improve regio- and stereoselectivities in the syntheses of macromolecules and natural products.[1] Its principle lies in the constraint of two reacting components within a short distance (A and B in Fig. 1a), which magnifies the effective concentration of the reactants and stabilizes the transition-state (TS) structures, speeding up the reaction usually with increased or different selectivities compared with the intermolecular counterparts. However, many tethers developed thus far have a sizable freedom of internal motion, permitting the formation of a number of transient structures besides the near-TS structures during the reactions. To diminish potential side-product formation, one may need a tether with a restricted and discontinuous motion. A molecular hinge is one that enables this kind of motion; *i.e.*, the switch between an open structure and a closed near-TS structure as shown in Fig. 1b.

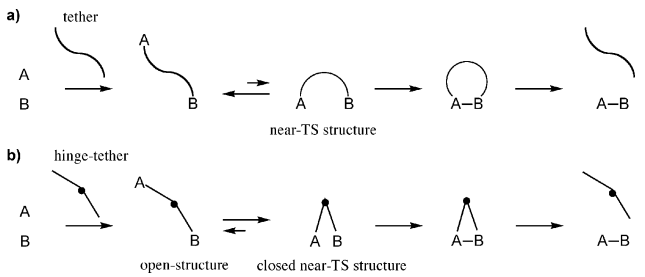

Fig. 1 A coupling reaction between **A** and **B** assisted by a general tether (a) and by a hinge-like tether (b).

Although two reactants are far apart in the open structure so that the tether-attachment is easy, the closed hinge can be a scaffold to stabilize the near-TS structure.

We have developed hinge-like molecules employing the ring flip of β-xylopyranosides (Fig. 2).[2] A β-xylopyranoside adopting the $^4C_1$ chair conformation is regarded as an open-hinge, because all the substituents are equatorially oriented and, if the molecular components are attached to the 1,3- or 2,4-positions, they will form an extended arrangement. On the other hand, when the same xylopyranoside adopts a $^1C_4$ conformation, it resembles a closed-hinge and the molecular components at the 1,3- or 2,4-positions are arranged in a stacked manner because the substituents are now all in an axial orientation. In practice, when pyrene groups were incorporated into the 2,4-positions of methyl β-xylopyranoside, pyrene-stacking was made possible by this hinge-like motion.[3] The population of the closed form was solvent-dependent and thus we were able to open and close the hinge molecule by simply changing solvents. These results prompted us to investigate the use of the hinge molecule in the tethering system for the [2 + 2] cycloaddition of cinnamate. This cycloaddition was selected as a model reaction to evaluate the hinge tether because there are a number of examples of tethered syntheses for comparison with this reaction.[4] In addition, the diaxial scaffold provided by the hinge-tether seemed to fit the product-like TS structure of the cycloaddition, which was assumed to be a stacked dimer of two cinnamates.

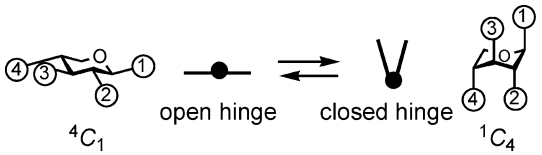

Fig. 2 A β-xylopyranoside as a hinge molecule.

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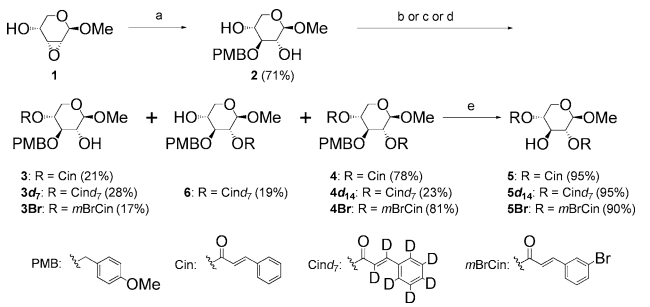
Results and discussion

At first, we attempted to tether two cinnamates by the direct and selective esterification of methyl xylopyranoside in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), 4-(dimethylamino)pyridine (DMAP), and cinnamic acid. However, the desired 2,4-dicinnamate was obtained in only 3 to 5% yields in DMF, pyridine, or toluene–pyridine, while all the other possible isomers were produced at higher yields. We thus decided to block the 3-OH group with a temporary protecting group. We synthesized methyl 3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside **2** from the epoxide **1** through nucleophilic ring opening with *p*-methoxybenzyloxide (Scheme 1).[5] Although the ^{1}H NMR spectrum of **2** is complicated due to the overlap of H2 and H3 signals, the coupling constants of $J_{4,5a} = 5.3$ Hz and $J_{4,5b} = 10$ Hz are typical of the $^4C_1$ conformation, indicating that **2** sits in the "open-form". Esterification of *p*-methoxybenzyl ether **2** was performed with cinnamic acid, EDC, and DMAP to give 3-*O*-protected dicinnamate **4** in 78% yield. In this reaction, 4-monocinnamate **3** was also obtained in 21% yield. The coupling constants of compounds **3** and **4** were deduced to be 19% and 51% (Table 1) of the $^1C_4$ populations, respectively, by previously reported methods.[2] A higher $^1C_4$ population of **4** than **3** is most likely due to stabilization caused by aromatic stacking (Fig. 3). Deprotection of the 3-*O*-*p*-methoxybenzyl group of compound **4** was carried out with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to give the desired 2,4-dicinnamate **5**. The $^1C_4$ population of compound **5** and 2,4-dipyrenecarbonyl derivative had a similar solvent-dependence:[3] 70%, 23%, and 22%, respectively for $CDCl_3$, CD_3OD, and DMSO-d_6 solutions, indicating that less polar solvents tend to afford a greater population of the closed-form. Solvent dependence has been attributed to the disturbance of a hydrogen bond by a polar solvent and to aromatic stacking that stabilizes the closed-hinge in a non-polar solvent, as suggested for the 2,4-dipyrenecarbonyl derivative.[3] The fact that there is a smaller $^1C_4$ population of 3-*O*-protected hinge **4** (51%) than the deprotected counterpart **5** (70%) emphasizes the importance of the hydrogen bond between 3-OH and 1-O in the stabilization of the closed form. The following profiles can be drawn from the above results: cinnamates are readily attachable to the uncrowded open form of the hinge-tether. Immediately after attachment, the hinge-tether automatically closes in 50% of the population. Further closure of the hinge-tether is enhanced by the removal of the 3-OH blocking group and by dissolving it in a non-polar solvent.



Scheme 1 Synthesis of 2,4-dicinnamate derivatives of methyl 3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside (**2**). Reagents and conditions: (a) PMBO$^-$Na$^+$; (b) CinOH, EDC, DMAP; (c) Cind_7OH, SO_2Cl_2, TEA; (d) *m*BrCinOH, EDC, DMAP; (e) DDQ.

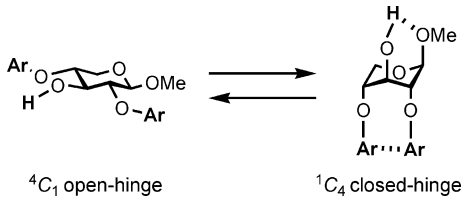
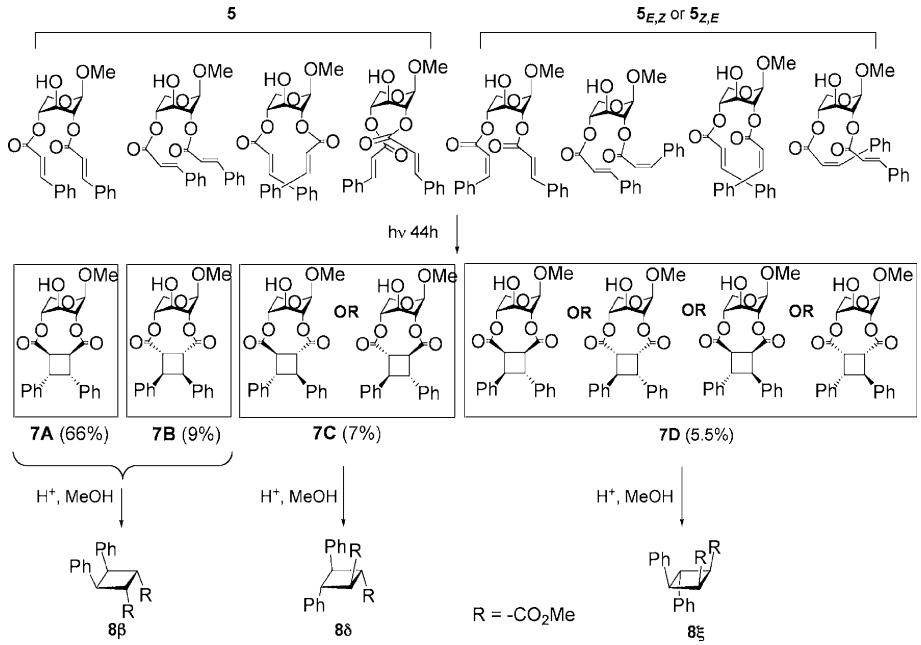


Fig. 3 Importance of aromatic stacking and hydrogen bonding for the formation of the closed-hinge.

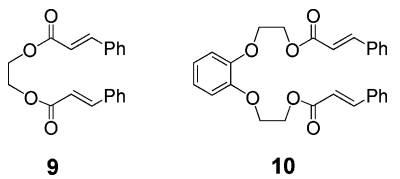
Table 1 *J*-Values (Hz) and $^1C_4$ population of xylopyranoside derivatives

Compound	Solvent	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5b}$	$^1C_4$
2	$CDCl_3$	—	—	—	5.3	10.2	0%
3	$CDCl_3$	6.7	8.5	8.5	5.2	8.9	19%
4	$CDCl_3$	4.7	6.1	6.1	3.8	6.1	51%
5	$CDCl_3$	3.7	5.3	5.3	3.4	4.6	70%
5	CD_3OD	6.6	8.4	8.4	4.7	8.5	23%
5	DMSO-d_7	7.3	8.6	8.6	5.2	7.8	22%

We next undertook a [2 + 2] cycloaddition for the two cinnamates of compound **5** to assess whether the closed-form of the hinge-tether allows for an intramolecular coupling reaction. Solutions of **5** in $CHCl_3$, methanol or DMF were photoirradiated at 313 nm with a band-filtered 500 W Hg(Xe) lamp. Only the $CHCl_3$ solution underwent a reaction. Disappearance of compound **5** was confirmed after 44 h by UV absorption at 270 nm and the reaction resulted in a mixture of four diastereomers **7A**–**D**, which were partially isolated by silica gel column chromatography. From the integrals in the ^{1}H NMR spectra, the yields of **7A**–**D** were determined to be 66%, 9%, 7%, and 5.5%, respectively. Since determination of the stereochemistry of these compounds by ^{1}H NMR spectra seemed impractical, the product mixture was transesterified with methanol to remove the hinge-tether. The fractions including **7A** and **7B** diastereomers produced an identical cyclobutane, whose structure was elucidated to be methyl β-truxinate **8**β by comparison with the reported ^{1}H NMR spectrum.[6] This result indicates that two major tethered adducts have the structures **7A** and **7B** shown in Scheme 2, in which the hinge-tether was connected in different orientations. Molecular models suggest that **7B** is more congested than **7A** with regard to the space between the benzene rings and the equatorial protons of H1 and H5 (Fig. 4), accounting for the large downfield shifts of H1 and H5b in the ^{1}H NMR spectrum of the cycloadduct **7B** owing to ring current effects. A fraction containing three products (**7A**, **7C** and **7D**) produced methyl β-, δ-, and ξ-truxinates on transesterification. However, we could not determine the stereochemistry of **7C** out of two possible diastereomers and **7D** out of four possible diastereomers. Overall, the product ratio of methyl β-, δ-, and ξ-truxinates (**8**β, δ, ξ) in this hinge-tethered synthesis was 86 : 8 : 6. All the isomers are head-to-head adducts derived from **5** with the β- and δ-isomers being *E*–*E* adducts and the ξ-isomer being a *E*–*Z* adduct as shown in Scheme 2. The regio- and stereoselectivities are comparable to those reported by others for tethered cinnamates,[4] though a few studies demonstrated the exclusive formation of β- and δ-truxinates from the tethered dicinnamates **9**[7] and **10**,[8] respectively (Chart 1). Though the ξ-isomer is asymmetric, we were unable to elucidate the stereochemistry because neither the tethered-cycloadduct **7D** nor the released-cycloadduct **8**ξ could be separated from the other diastereomers. The production of



Scheme 2



9 **10**

Chart 1

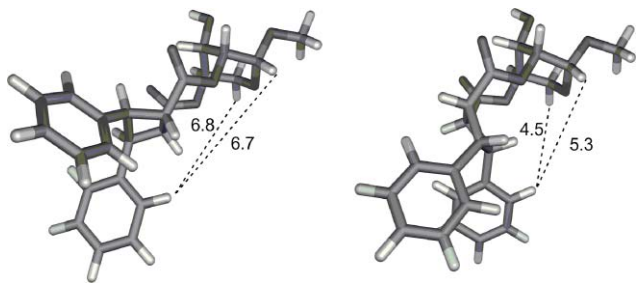
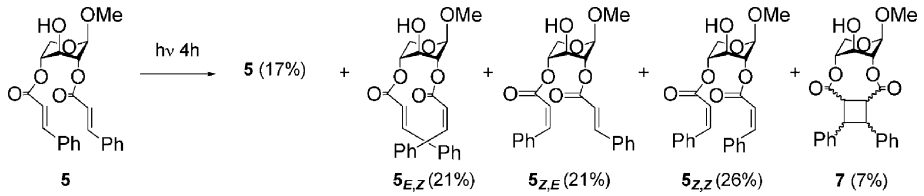


Fig. 4 Molecular models of compounds **7A** (left) and **7B** (right). Numerals are lengths in angstrom between H1 or H5b and the nearest peripheral proton of a benzene ring. The molecular models were optimized by SYBYL force field using PC Spartan software.[11]

ξ-truxinate is rather unusual, since this isomer has been produced in small quantities in non-tether reactions[9] and has seldom been obtained from tethered cinnamates.[10] This isomer, and even some of the other isomers, might have been produced in an intermolecular cycloaddition. To assess this hypothesis, the cinnamates of **5** were replaced with the all-deuterated cinnamates. This would facilitate the assignment of the pyranose protons in the ^{1}H NMR spectra and thus the determination of the ring conformation as to whether it is fixed in $^1C_4$ or unfixed in a conformational equilibrium. The di-d_7-cinnamate **5**d_{14} was prepared by subjecting compound **2** to thionyl chloride, triethylamine, and cinnamic acid-d_7 and the subsequent removal of the *p*-methoxybenzyl group (Scheme 1). The esterification resulted in an incomplete reaction to give two mono-cinnamates, **6** and **3**d_7, besides dicinnamate **4**d_{14}. The esterification conditions used for the synthesis of compound **4** (EDC, DMAP) resulted in the exchange of D to H at the α-position of the cinnamate. The conformation of **5**d_{14} showed almost the same solvent dependence as that of **5** and photoirradiation was performed for the chloroform solution of **5**d_{14} under the same conditions as those for **5**. The reaction produced four products **7**d_{14}**A**–**D** in 75% yield with a product ratio of 65 : 13 : 11 : 11. The stereoselectivity (β–δ–ξ = 78 : 11 : 11) was similar to that obtained with the all-H cycloadduct **7**. These isomers had singlet H1 signals in the ^{1}H NMR spectra indicative of a $^1C_4$ pyranose conformation. According to our observations, all the β-xylopyranosides fixed in $^1C_4$ showed singlet H-1 signals and they became doublets when they were unfixed even with 75% $^1C_4$ population.[2,3] It was thus suggested that all the diastereomers were produced through intramolecular cycloaddition.

During the photoirradiation study, we found that there was a pre-equilibrium of the double-bond isomerization prior to cyclization to afford *Z*–*Z* **5**$_{Z,Z}$ (26%), *E*–*Z* **5**$_{E,Z}$ (21%), and *Z*–*E* **5**$_{Z,E}$ (21%) dicinnamates, together with the cycloadducts **7** (7%) and the recovery of **5** (17%) after 4 h photoirradiation (Scheme 3). Though the isomers could not be isolated and complete conformational analyses were unfeasible due to the signal overlaps in the ^{1}H NMR spectra, the larger *J*-values of H1 signals for **5**$_{Z,Z}$ (5.2 Hz), **5**$_{E,Z}$, and **5**$_{Z,E}$ (4.4 and 4.7 Hz) relative to **5** (3.7 Hz) indicate that the incorporation of *Z*-cinnamate tends to reduce the $^1C_4$ population. We thus postulate that the formation of the near-TS structure is relatively difficult from *Z*-cinnamates[12] probably due to congestion, and therefore the formation of an *E*–*E* adduct was favored despite a small proportion of precursor **5** during the double-bond isomerization.

Nakatsuji and coworkers found that the [2 + 2] cycloaddition of *m*-bromocinnamates results exclusively in the *E*–*E* adducts.[13] The



Scheme 3

excellent stereoselectivity is explained by the reactivity–selectivity principle, where the electron-withdrawing group caused the lower reactivity and higher selectivity compared to the non-substituted cinnamate. To ensure that our tether system reproduces high selectivity, we synthesized the hinge-tethered *m*-bromocinnamate **5Br** from compound **2** through compound **4Br** (Scheme 1). Photoirradiation of **5Br** was carried out under the same conditions as for **5** to afford **7BrA** and **7BrB** in 67% and 4% yields, respectively. The other adducts were not found in this case. Release of the hinge unit from the mixture of **7BrA** and **7BrB** yielded only the methyl β-truxinate derivative (**8Br**β). The stereochemistry of **8Br**β was determined by the similarity of its NMR spectra with that of **8**β. These results demonstrate that the hinge-tether system affords a practical stereoselectivity in cases where an appropriate substrate is attached to the tether.

Conclusions

We developed a novel hinge-type tether for the [2 + 2] cycloaddition of cinnamate, in which a two-step closing procedure is employed as shown in Fig. 5. The cinnamates were feasibly incorporated into the partially protected hinge sugar in a polar solvent, since the hinge molecule is mostly opened and uncrowded. Deprotection (1st stage) and the use of a non-polar solvent (2nd stage) promote the closure of the hinge molecule with the assistance of hydrogen-bonding and aromatic stacking. The [2 + 2] cycloaddition of hinge-tethered cinnamates proceeded efficiently with this closed scaffold in a stereoselective manner. The use of *m*-bromocinnamates afforded β-truxinate exclusively after removal from the hinge molecule. Overall, the carbohydrate-tether can intentionally generate a switching motion between open (or uncrowded) and closed (or near-transition-state) forms, providing a conceptually new tethering system.

Experimental

General

All solvents and reagents used were reagent grade and, in cases where further purification was required, standard procedures[14] were followed. Solution transfers where anhydrous conditions were required were done under dry argon using syringes. Thin-layer chromatograms (TLC) were performed on precoated silica gel Merck 60-F254 plates (Art 5715) and visualized by quenching of fluorescence and/or by charring after spraying with 1% $CeSO_4$–1.5% $(NH_4)6Mo_7O_{24}{\cdot}4H_2O$–10% H_2SO_4. Column chromatography was performed on Merck Kieselgel 60 (Art 7734), Wako gel C-300, or Kanto Silica gel 60N (spherical, neutral) with the solvent systems specified

Optical rotations were determined with a Horiba SEPA-200 using 1 dm or 0.1 dm length cell. ^{1}H NMR (1D, COSY, HMQC, and HMBC) spectra were recorded at 400 MHz (Varian Unity-400) or 270 MHz (JEOL EX-270). Internal tetramethylsilane (δ 0 ppm) was used as a standard in $CDCl_3$ or solvents peaks were used as standards (δ 2.50 ppm in DMSO-d_6 or δ 2.75 in DMF-d_7). Chemical shifts are expressed in ppm referenced to the solvent, as an internal standard. Coupling constants are measured in Hz. The multiplicity of signals is abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, ddd = doublet of doublets of doublets, br = broad signal, m = multiplet. ^{13}C NMR spectra were recorded at 67.8 MHz (JEOL JNM-EX-270) or 100.6 MHz (Varian Unity-400) and solvent peaks were used as standards (δ 77.0 ppm in $CDCl_3$ or δ 29.76 in DMF-d_7). High resolution mass spectra (HRMS) were recorded on Mariner Biospectrometry Workstation ESI-TOF MS.

Methyl 3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside, 2. A mixture of 55% NaH (75 mg, 1.71 mmol), which was washed several times with hexane to remove the coated oil prior to use,

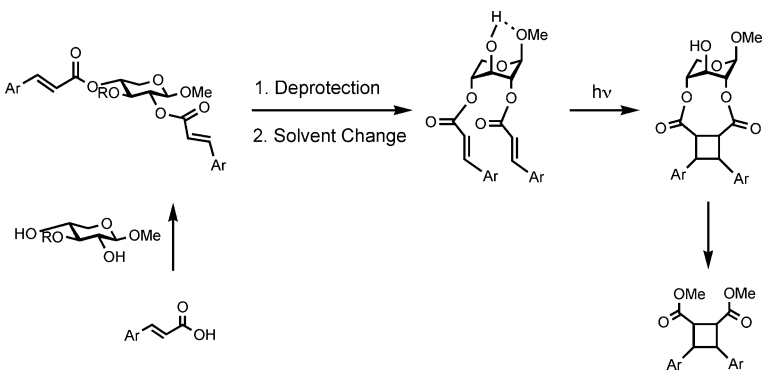


Fig. 5 The two-step closing system for the hinge-tethered photocycloaddition of cinnamates.

and *p*-methoxybenzyl alcohol (2.1 mL, 16.8 mmol) was stirred for 15 min at 0 °C. To this suspension was dropped a solution of methyl 2,3-anhydro-β-D-ribopyranoside (**1**, 50 mg, 0.342 mmol) in THF (2 mL) and the mixture was stirred for 50 min at room temperature and 3.5 h at 70 °C. The mixture was poured into ice-water and extracted with $CHCl_3$. The organic layer was washed successively with aqueous NH_4Cl and brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica-gel column chromatography (hexane–ethyl acetate, 3 : 1 to 2 : 3) to give **2** (69 mg, 71%) as a white solid: R_f 0.15 (hexane–ethyl acetate, 1 : 1), mp 140–143 °C; $[\alpha]_D^{22}$ −37.6 (*c* 1.00 in MeOH); δ_H (270 MHz, CD_3OD) 7.35 (2H, d, *J* 8.8, Ar), 6.87 (2H, d, *J* 8.8, Ar), 4.81 (1H, d, *J* 11.2, C*H*$_2$Ph), 4.78 (1H, d, *J* 11.2, C*H*$_2$Ph), 4.13 (1H, d, *J* 7.5, 1-H), 3.86 (1H, dd, *J* 11.4, *J* 5.3, 5-Ha), 3.78 (3H, s, PhOMe), 3.63–3.37 (1H, m, 4-H), 3.49 (3H, s, OMe), 3.32–3.27 (2H, m, 2-H, 3-H), 3.21 (1H, dd, *J* 11.4, *J* 10.2, H-5b); δ_C (67.8 MHz, CD_3OD) 160.7, 132.3, 130.8, 130.7, 114.7, 114.5, 106.2 (C1), 85.4, 75.5 (CH_2Ph), 74.8, 71.1 (C4), 66.9 (C5), 57.2 (Me), 55.7 (Me); HRMS (ESI) Found: 307.1172 $[M + Na]^+$. Calc. for $C_{14}H_{20}O_6Na$ 307.1158.

Methyl 2,4-di-*O*-(*E*)-cinnamoyl-3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside, 4. A solution of cinnamic acid (70 mg, 0.472 mmol) and $SOCl_2$ (138 μL, 1.89 mmol) in dry toluene (2.5 mL) was stirred for 2 h at 80 °C. After the solution was evaporated, the residue was dried under vacuum for 1 h and dissolved in CH_2Cl_2 (1.0 mL), to which was added a solution of compound **2** (45 mg, 0.158 mmol) in CH_2Cl_2–pyridine (2 : 1, 1.5 mL) at 0 °C. The solution was stirred for 2 h at room temperature and then 2 h at 40 °C. The mixture was poured into ice-water and extracted with $CHCl_3$. The organic layer was washed successively with aqueous NH_4Cl, aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica-gel column chromatography (hexane–ethyl acetate, 4 : 1 to 2 : 1) to give methyl 4-*O*-(*E*)-cinnamoyl-3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside (**3**, 14 mg, 21%) and 2,4-dicinnamate **4** (67 mg, 78%) as solids.

3. R_f 0.26 (hexane–ethyl acetate, 3 : 2); mp 113–115 °C; $[\alpha]_D^{22}$ −48.2 (*c* 0.45 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.67 (1H, d, *J* 16.0Hz, Ph*H*C=C), 7.54–7.50 (2H, m, Ar), 7.42–7.38 (3H, m, Ar), 7.27–7.24 (2H, m, Ar), 6.84–6.81 (2H, m, Ar), 6.36 (1H, d, *J* 16.0, CO*H*C=C), 5.05 (1H, ddd, $J_{3,4}$ 8.5, $J_{4,5a}$ 5.2, $J_{4,5b}$ 8.9, 4-H), 4.73 (2H, s, C*H*$_2$Ph), 4.25 (1H, d, $J_{1,2}$ 6.7, 1-H), 4.15 (1H, dd, $J_{4,5a}$ 5.2, $J_{5a,5b}$ 11.7, 5-Ha), 3.72 (3H, s, PhOMe), 3.63 (1H, t, *J* 8.5, 3-H), 3.61–3.56 (1H, bt, 2-H), 3.54 (3H, s, OMe), 3.31 (1H, dd, $J_{4,5b}$ 8.9, $J_{5a,5b}$ 11.7, 5-Hb), 2.51 (1H, b, OH); δ_C (67.8 MHz, $CDCl_3$) 166.0 (C=O), 146.0, 134.4, 130.8, 130.5, 129.8, 129.2, 128.4, 117.5, 114.1, 104.2 (C1), 80.0 (C3), 74.0 (*C*H$_2$Ph), 73.5 (C2), 71.3 (C4), 62.8 (C5), 57.1 (Me), 55.4 (Me); HRMS (ESI) Found: 437.1578 $[M + Na]^+$. Calc. for $C_{23}H_{26}O_7Na$ 437.1576.

4. R_f 0.24 (hexane–ethyl acetate, 3 : 1); mp 125–127 °C; $[\alpha]_D^{22}$ −78.3 (*c* 0.635 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.73 (1H, d, *J* 16.0, Ph*H*C=C), 7.69 (1H, d, *J* 16.5, Ph*H*C=C), 7.49–7.44 (4H, m, Ar), 7.41–7.29 (6H, m, Ar), 7.26–7.23 (2H, m, Ar), 6.82–6.79 (2H, m, Ar), 6.43 (1H, d, *J* 16.0, CO*H*C=C), 6.40 (1H, d, *J* 16.5, CO*H*C=C), 5.15 (1H, dd, $J_{1,2}$ 4.7, $J_{2,3}$ 6.1, 2-H), 5.05 (1H, ddd, $J_{3,4}$ 6.2, $J_{4,5a}$ 3.8, $J_{4,5b}$ 6.1, 4-H), 4.69 (1H, d, *J* 11.8, C*H*$_2$Ph), 4.64 (1H, d, *J* 11.8, C*H*$_2$Ph), 4.58 (1H, d, $J_{1,2}$ 4.7, 1-H), 4.27 (1H, dd, $J_{4,5a}$ 3.8, $J_{5a,5b}$ 12.1, 5-Ha), 3.82 (1H, t, *J* 6.2, 3-H), 3.69 (3H, s, PhOMe), 3.53 (1H, dd, $J_{4,5b}$ 6.1, $J_{5a,5b}$ 12.1, 5-Hb), 3.48 (3H, s, OMe); δ_C (67.8 MHz, $CDCl_3$) 165.7 (C=O), 165.3 (C=O), 159.1, 145.6, 145.6, 134.0, 134.0, 134.0, 130.4, 130.3, 129.7, 129.5, 128.8, 128.8, 128.1, 128.0, 117.4, 113.7, 100.7 (C1), 75.2 (C3), 72.6 (*C*H$_2$Ph), 70.3 (C2), 69.7 (C4), 60.5 (C5), 56.3 (Me), 55.1 (Me); HRMS (ESI) Found: 567.1999 $[M + Na]^+$. Calc. for $C_{32}H_{32}O_8Na$ 567.1995.

Methyl 2,4-di-*O*-(*E*)-cinnamoyl-β-D-xylopyranoside, 5. To a stirred solution of compound **4** (84 mg, 0.154 mmol) in CH_2Cl_2–H_2O (18 : 1, 5 mL) was added 2,3-dicholoro-5,6-dicyano-1,4-benzoquinone (DDQ; 40 mg, 0.176 mmol) at 0 °C and the mixture was further stirred for 9 h at room temperature. The mixture was diluted with $CHCl_3$–H_2O and the organic layer was washed with sat. $NaHCO_3$ and then brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica-gel column chromatography (hexane–ethyl acetate, 6 : 1 to 5 : 2) to give compound **5** (62 mg, 95%) as an amorphous solid: R_f 0.16 (hexane–ethyl acetate, 3 : 1); mp 56–58 °C; $[\alpha]_D^{22}$ −41.5 (*c* 1.27 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.77 (1H, d, *J* 16.0, Ph*H*C=C), 7.75 (1H, d, *J* 16.5, Ph*H*C=C), 7.44–7.25 (10H, m, Ar), 6.48 (1H, d, *J* 16.0, CO*H*C=C), 6.46 (1H, d, *J* 16.5, CO*H*C=C), 4.99–4.96 (2H, m, 2-H, 4-H), 4.74 (1H, d, $J_{1,2}$ 3.7, 1-H), 4.26 (1H, dd, $J_{4,5a}$ 3.4, $J_{5a,5b}$ 12.8, 5-Ha), 4.05 (1H, dt, $J_{2,3} = J_{3,4}$ 5.3, $J_{3,OH}$ 8.1, 3-H), 3.71 (1H, dd, $J_{4,5b}$ 4.6, $J_{5a,5b}$ 12.8, 5-Hb), 3.52 (3H, s, OMe), 3.25 (1H, d, $J_{3,OH}$ 8.1, OH); δ_H (400 MHz, CD_3OD) 7.76 (1H, d, *J* 16.0, Ph*H*C=C), 7.745 (1H, d, *J* 16.5, Ph*H*C=C), 7.60–7.57 (4H, m, Ar), 7.40–7.25 (6H, m, Ar), 6.56 (2H, d, *J* 16.0, CO*H*C=C × 2), 4.93–4.89 (2H, m, 2-H, 4-H), 4.53 (1H, d, $J_{1,2}$ 6.6, 1-H), 4.17 (1H, dd, $J_{4,5a}$ 4.7, $J_{5a,5b}$ 11.6, 5-Ha), 3.94 (1H, t, $J_{2,3} = J_{3,4}$ 8.4, 3-H), 3.48 (1H, dd, $J_{4,5b}$ 8.5, $J_{5a,5b}$ 11.6, 5-Hb), 3.47 (3H, s, OMe); δ_H (400 MHz, DMSO-d_6) 7.73–7.67 (6H, m, Ar, Ph*H*C=C × 2), 7.56–6.40 (6H, m, Ar), 6.66 (1H, d, *J* 16.0, CO*H*C=C), 6.65 (1H, d, *J* 16.0, CO*H*C=C), 5.69 (1H, d, $J_{3,OH}$ 5.9, OH), 4.82–4.76 (2H, m, 2-H, 4-H), 4.51 (1H, d, $J_{1,2}$ 7.3, 1-H), 4.02 (1H, dd, $J_{4,5a}$ 5.2, $J_{5a,5b}$ 11.6, 5-Ha), 3.82 (1H, dt, $J_{2,3} = J_{3,4}$ 8.6, $J_{3,OH}$ 5.9, 3-H), 3.41 (1H, dd, $J_{4,5b}$ 7.8, $J_{5a,5b}$ 11.6, 5-Hb), 3.37 (3H, s, OMe); δ_C (67.8 MHz, $CDCl_3$) 166.2 (C=O), 165.9 (C=O), 146.1, 145.9, 134.0, 134.0, 130.5, 130.5, 128.9, 128.1, 128.1, 117.4, 117.1, 99.9 (C1), 77.2, 70.4 (C4), 70.2 (C2), 68.2 (C3), 59.3 (C5), 56.2 (Me); HRMS (ESI) Found: 425.1635 $[M + H]^+$. Calc. for $C_{24}H_{25}O_7$ 425.1601.

Methyl 2,4-di-*O*-(*E*)-cinnamoyl-d_7-3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside, 4d_{14}. A solution of (*E*)-cinnamic-d_7 acid (60 mg, 0.387 mmol) and $SOCl_2$ (231 μL, 3.17 mmol) in dry toluene (2.5 mL) was stirred for 2 h at 80 °C. After the solution was evaporated, the residue was dried under vacuum for 1 h and dissolved in CH_2Cl_2 (1.5 mL). In parallel, compound **2** (50 mg, 0.176 mmol) was co-evaporated with D_2O–acetone-d_6 (1 : 1) and dissolved in CH_2Cl_2–pyridine (2 : 1, 1.5 mL). The solution of **2** was carefully added to the cinnamic-d_7 chloride solution at 0 °C. The mixture was further stirred for 1 h at room temperature and then for 24 h at 40 °C. The mixture was poured into ice-water and extracted with $CHCl_3$. The organic layer was washed successively with aqueous NH_4Cl, aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica-gel column chromatography (hexane–ethyl acetate, 4 : 1 through 2 : 1 to 2 : 3) to give methyl 4-*O*-(*E*)-cinnamoyl-d_7-3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside (**3**d_7, 21 mg, 28%), 2,4-dicinnamate-d_7 **4**d_{14} (32 mg, 33%), and methyl

2-*O*-(*E*)-cinnamoyl-d_7-3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside (**6**, 14 mg, 19%) as solids.

3d_7. R_f 0.26 (hexane–ethyl acetate, 1.5 : 1); mp 113–115 °C; $[a]_D^{22}$ −88.6 (*c* 0.525 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.28–7.24 (2H, m, Ar), 6.85–6.81 (2H, m, Ar), 5.06 (1H, dt, $J_{4,5a}$ 5.2, $J_{3,4}$ = $J_{4,5b}$ 8.9, 4-H), 4.73 (2H, s, CH_2Ph), 4.26 (1H, d, $J_{1,2}$ 6.7, 1-H), 4.15 (1H, dd, $J_{4,5a}$ 5.2, $J_{5a,5b}$ 11.8, 5-Ha), 3.72 (3H, s, PhOMe), 3.64 (1H, t, $J_{2,3}$ = $J_{3,4}$ 8.9, 3-H), 3.58 (1H, bt, 2-H), 3.54 (3H, s, Me), 3.31 (1H, dd, $J_{4,5b}$ 8.9, $J_{5a,5b}$ 11.8, H-5b), 2.47 (1H, b, OH); δ_C (67.8 MHz, $CDCl_3$) 165.8 (C=O), 159.3, 133.8, 130.2, 130.0, 129.6, 128.8, 128.4, 128.1, 127.7, 127.4, 113.8, 104.0 (C1), 79.8 (C3), 77.2, 73.8 (*C*H_2Ph), 73.3 (C2), 71.0 (C4), 62.6 (C5), 57.0 (Me), 55.1 (Me); HRMS (ESI) Found: 444.2000 $[M + Na]^+$. Calc. for $C_{23}H_{19}D_7O_7Na$ 444.2016.

4d_{14}. R_f 0.24 (hexane–ethyl acetate, 3 : 1); mp 124–126 °C; $[a]_D^{22}$ −47.4 (*c* 0.515 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.26–7.23 (2H, m, Ar), 6.82–6.79 (2H, m, Ar), 5.10 (1H, dd, $J_{1,2}$ 4.7, $J_{2,3}$ 6.3, 2-H), 5.05 (1H, dt, $J_{4,5a}$ 3.8, $J_{3,4}$ = $J_{4,5b}$ 6.3, 4-H), 4.69 (1H, d, *J* 11.8, CH_2Ph), 4.65 (1H, d, *J* 11.8, CH_2Ph), 4.58 (1H, d, $J_{1,2}$ 4.7 Hz, 1-H), 4.26 (1H, dd, $J_{4,5a}$ 3.8, $J_{5a,5b}$ 12.2, 5-Ha), 3.82 (1H, t, $J_{2,3}$ = $J_{3,4}$ 6.3, 3-H), 3.69 (3H, s, PhOMe), 3.54 (1H, dd, $J_{4,5b}$ 6.3, $J_{5a,5b}$ 12.2, 5-Hb), 3.48 (3H, s, OMe); δ_C (67.8 MHz, $CDCl_3$) 166.1 (C=O), 165.7 (C=O), 159.4, 134.0, 129.8, 128.6, 127.9, 127.7, 117.5, 113.9, 101.0 (C1), 75.4 (C3), 72.9 (*C*H_2Ph), 70.4 (C2), 69.9 (C4), 60.7 (C5), 56.5 (Me), 55.3 (Me); HRMS (ESI) Found: 581.2851 $[M + Na]^+$. Calc. for $C_{32}H_{18}D_{14}O_8Na$ 581.2873.

6. R_f 0.19 (hexane–ethyl acetate, 1.5 : 1); mp 62–64 °C; $[a]_D^{22}$ −2.6 (*c* 0.38 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.26–7.22 (2H, m, Ar), 6.86–6.82 (2H, m, Ar), 5.08 (1H, dd, $J_{1,2}$ 6.0, $J_{2,3}$ 7.5, 2-H), 4.72 (1H, d, *J* 11.5, CH_2Ph), 4.56 (1H, d, *J* 11.5, CH_2Ph), 4.44 (1H, d, $J_{1,2}$ 6.0, 1-H), 4.10 (1H, dd, $J_{4,5a}$ 4.3, $J_{5a,5b}$ 11.6, 5-Ha), 3.81–3.72 (1H, m, 4-H), 3.74 (3H, s, PhOMe), 3.56 (1H, t, $J_{2,3}$ = $J_{3,4}$ 7.5, 3-H), 3.47 (3H, s, OMe), 3.37 (1H, dd, $J_{4,5b}$ 8.1, $J_{5a,5b}$ 11.6, 5-Hb), 2.40 (1H, b, OH); δ_C (67.8 MHz, $CDCl_3$) 165.7 (C=O), 159.6, 134.1, 130.2, 129.9, 117.4, 114.2, 102.0 (C1), 80.2 (C3), 77.4, 73.6 (*C*H_2Ph), 71.8 (C2), 69.0 (C4), 64.1 (C5), 56.7 (Me), 55.4 (Me); HRMS (ESI) Found: 444.2013 $[M + Na]^+$. Calc. for $C_{23}H_{19}D_7O_7Na$ 444.2016.

Methyl 2,4-di-*O*-(*E*)-cinnamoyl-d_7-β-D-xylopyranoside, 5d_{14}. To a stirred solution of **4**d_{14} (31.0 mg, 0.055 mmol) in CH_2Cl_2–H_2O (18 : 1, 1.0 mL) was added DDQ (14 mg, 0.62 mmol) at 0 °C and the mixture was further stirred for 11 h at room temperature. The mixture was diluted with $CHCl_3$–H_2O and the organic layer was washed with sat. $NaHCO_3$ and then brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica-gel column chromatography (hexane–ethyl acetate, 6 : 1 to 5 : 2) to give compound **5**d_{14} (23 mg, 95%) as an amorphous solid: R_f 0.30 (hexane–ethyl acetate, 2 : 1); mp 56–58 °C; $[a]_D^{22}$ −42.6 (*c* 1.00 in $CHCl_3$); δ_H (270 MHz, $CDCl_3$) 5.00–4.96 (2H, m, 2-H, 4-H), 4.74 (1H, d, $J_{1,2}$ 3.7, 1-H), 4.26 (1H, dd, $J_{4,5a}$ 3.6, $J_{5a,5b}$ 12.8, 5-Ha), 4.05 (1H, b, 3-H), 3.70 (1H, dd, $J_{4,5b}$ 4.1, $J_{5a,5b}$ 12.8, 5-Hb), 3.52 (3H, s, OMe), 3.29 (1H, b, OH); δ_C (67.8 MHz, $CDCl_3$) 166.2 (C=O), 165.9 (C=O), 146.0, 145.7, 145.4, 133.7, 128.7, 128.3, 128.0, 127.7, 127.4, 117.0, 99.9 (C1), 70.4, 70.2, 68.2 (C3), 59.3 (C5), 56.2 (Me); HRMS (ESI) Found: 461.2280 $[M + Na]^+$. Calc. for $C_{24}H_{10}D_{14}O_7Na$ 461.2298.

Methyl 2,4-di-*O*-(*E*)-3-bromocinnamoyl-3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside, 4Br. A mixture of **2** (100 mg, 0.352 mmol), 3-bromocinnamic acid (176 mg, 0.775 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC; 148 mg, 0.772 mmol) and 4-(dimethylamino)pyridine (DMAP; 95 mg, 0.778 mmol) in DMF (3.5 mL) was stirred for 24 h at room temperature. The mixture was poured into ice-water and extracted with $CHCl_3$. The organic layer was washed successively with 0.5 M HCl, aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica-gel column chromatography (hexane–ethyl acetate, 7 : 2 to 2 : 1) to give methyl 4-*O*-(*E*)-3-bromocinnamoyl-3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside (**3Br**, 29 mg, 17%) as a solid and 2,4-dicinnamate **4Br** (199 mg, 80%) as a syrup.

3Br. R_f 0.375 (hexane–ethyl acetate, 1 : 1); mp 148–150 °C; $[a]_D^{22}$ −40.7 (*c* 0.625 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.67–7.24 (7H, m, Ar, Ph*H*C=C × 2), 6.84–6.81 (2H, m, Ar), 6.33 (1H, d, *J* 16.0, CO*H*C=C), 5.05 (1H, ddd, $J_{3,4}$ 6.9, $J_{4,5a}$ 5.3, $J_{4,5b}$ 9.1, 4-H), 4.75 (1H, d, *J* 12.5, CH_2Ph), 4.70 (1H, d, *J* 12.5, CH_2Ph), 4.25 (1H, d, $J_{1,2}$ 6.3 Hz, 1-H), 4.14 (1H, dd, $J_{4,5a}$ 5.3, $J_{5a,5b}$ 11.7, 5-Ha), 3.73 (3H, s, PhOMe), 3.62 (1H, t, $J_{2,3}$ = $J_{3,4}$ 6.9, 3-H), 3.62–3.57 (1H, m, 2-H), 3.54 (3H, s, OMe), 3.30 (1H, dd, $J_{4,5b}$ 9.1, $J_{5a,5b}$ 11.7, 5-Hb), 2.45 (1H, b, OH); δ_C (67.8 MHz, $CDCl_3$) 165.4 (C=O), 159.3, 143.9, 136.2, 133.3, 130.8, 130.4, 130.2, 129.7, 126.8, 123.1, 118.8, 113.8, 104.0 (C1), 79.8 (C3), 73.8 (*C*H_2Ph), 73.3 (C2), 71.1 (C4), 62.6 (C5), 56.9 (Me), 55.2 (Me); HRMS (ESI) Found: 515.0710 $[M + Na]^+$. Calc. for $C_{23}H_{25}O_7BrNa$ 515.0682.

4Br. R_f 0.34 (hexane–ethyl acetate, 2 : 1); $[a]_D^{22}$ −30.0 (*c* 2.34, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.63–6.17 (12H, m, Ar, Ph*H*C=C × 2), 6.82–6.78 (2H, m, Ar), 6.37 (1H, d, *J* 16.2, CO*H*C=C), 6.37 (1H, d, *J* 16.2, CO*H*C=C), 5.10 (1H, dd, $J_{1,2}$ 5.1, $J_{2,3}$ 6.6, 2-H), 5.06 (1H, ddd, $J_{3,4}$ 6.6, $J_{4,5a}$ 4.0, $J_{4,5b}$ 6.8, 4-H), 4.65 (2H, s, CH_2Ph), 4.54 (1H, d, $J_{1,2}$ 5.1, H-1), 4.25 (1H, dd, $J_{4,5a}$ 4.0, $J_{5a,5b}$ 12.0, 5-Ha), 3.81 (1H, t, $J_{2,3}$ = $J_{3,4}$ 6.6, 3-H), 3.69 (3H, s, PhOMe), 3.49 (1H, dd, $J_{4,5b}$ 6.8, $J_{5a,5b}$ 12.0 Hz, 5-Hb), 3.48 (3H, s, OMe); δ_C (67.8 MHz, $CDCl_3$) 165.3 (C=O), 164.9 (C=O), 159.2, 143.9, 143.8, 136.2, 136.1, 133.3, 133.2, 130.7, 130.4, 130.4, 129.7, 129.5, 126.7, 126.6, 123.0, 123.0, 118.9, 118.8, 113.7, 100.9 (C1), 75.7 (C3), 72.8 (*C*H_2Ph), 70.8 (C2), 70.1 (C4), 60.7 (C5), 56.2 (Me), 55.1 (Me); HRMS (ESI) Found: 723.0196 $[M + Na]^+$. Calc. for $C_{32}H_{30}O_8Br_2Na$ 723.0206.

Methyl 2,4-di-*O*-(*E*)-3-bromocinnamoyl-β-D-xylopyranoside, 5Br. To a stirred solution of **4Br** (182 mg, 0.258 mmol) in CH_2Cl_2–H_2O (18 : 1, 4 mL) was added DDQ (93 mg, 0.410 mmol) at 0 °C and the mixture was further stirred for 5 h at room temperature. The mixture was diluted with $CHCl_3$–H_2O and the organic layer was washed with sat. $NaHCO_3$ and then brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica-gel column chromatography (hexane–ethyl acetate, 5 : 1 to 5 : 2) to give compound **5Br** (135 mg, 90%) as a syrup: R_f 0.265 (hexane–ethyl acetate, 2 : 1); $[a]_D^{22}$ −28.1 (*c* 1.375 in $CHCl_3$); δ_H (270 MHz, $CDCl_3$) 7.65 (1H, d, *J* 15.9, Ph*H*C=C), 7.64 (1H, d, *J* 15.9, Ph*H*C=C), 7.584 (1H, s, 2-*H*-BrPh), 7.580 (1H, s, 2-*H*-BrPh), 7.476 (1H, d, *J* 7.8, 4-*H*-BrPh), 7.474 (1H, d, *J* 7.8, 4-*H*-BrPh), 7.328 (1H, d, *J* 7.8, 6-*H*-BrPh), 7.325 (1H, d, *J* 7.8, 6-*H*-BrPh), 7.172 (1H, d, *J* 7.8, 5-*H*-BrPh), 7.165 (1H, t, *J* 7.8, 5-*H*-BrPh), 6.44 (2H, d, *J* 15.9, CO*H*C=C × 2), 5.01–4.96 (2H, m, 2-H, 4-H), 4.69 (1H, d, $J_{1,2}$ 4.1, 1-H), 4.25 (1H, dd, $J_{4,5a}$ 3.5, $J_{5a,5b}$ 12.8, 5-Ha), 4.03 (1H, dt, $J_{2,3}$ = $J_{3,4}$ 5.3, $J_{3,OH}$ 7.9, 3-H), 3.66 (1H, dd, $J_{4,5b}$ 5.0, $J_{5a,5b}$ 12.8 Hz, 5-Hb), 3.50 (3H, s, OMe),

3.32 (1H, d, $J_{3,OH}$ 7.9 Hz, OH); δ_H (270 MHz, CD_3OD) 7.75 (2H, s, 2-*H*-BrPh), 7.68 (1H, d, *J* 16.0, Ph*H*C=C), 7.67 (1H, d, *J* 16.0, Ph*H*C=C), 7.55–7.53 (4H, m, Ar), 7.296 (1H, t, *J* 7.8, 5-*H*-BrPhh), 7.292 (1H, t, *J* 7.8, 5-*H*-BrPh), 6.69 (1H, d, *J* 16.0, CO*H*C=C), 6.68 (1H, d, *J* 16.0, CO*H*C=C), 4.93–4.88 (2H, m, 2-H, 4-H), 4.54 (1H, d, $J_{1,2}$ 6.6, 1-H), 4.17 (1H, dd, $J_{4,5a}$ 4.9, $J_{5a,5b}$ 11.7, 5-Ha), 3.95 (1H, t, $J_{2,3} = J_{3,4}$ 8.2, 3-H), 3.48 (1H, dd, $J_{4,5b}$ 8.6, $J_{5a,5b}$ 11.7, 5-Hb), 3.47 (3H, s, OMe); ^{1}H NMR (270 MHz, DMSO-d_6) 7.992 (1H, s, 2-*H*-BrPh), 7.987 (1H, s, 2-*H*-BrPh), 7.75 (2H, d, *J* 7.8, 4-*H*-BrPh), 7.68 (1H, d, *J* 16.0, Ph*H*C=C), 7.66 (1H, d, *J* 16.0, Ph*H*C=C), 7.62 (2H, d, *J* 7.8, 6-*H*-BrPh), 7.373 (1H, t, *J* 7.8, 5-*H*-BrPh), 7.368 (1H, t, *J* 7.8, 5-*H*-BrPh), 6.76 (1H, d, *J* 16.1, CO*H*C=C), 6.75 (1H, d, *J* 16.1, CO*H*C=C), 5.70 (1H, b, OH), 4.83–4.77 (1H, m, 4-H), 4.78 (1H, dd, $J_{1,2}$ 7.3, $J_{2,3}$ 8.7, 2-H), 4.51 (1H, d, $J_{1,2}$ 7.3, 1-H), 4.01 (1H, dd, $J_{4,5a}$ 6.1, $J_{5a,5b}$ 11.6, 5-Ha), 3.80 (1H, bt, 3-H), 3.46–3.34 (4H, m, 5-Hb, OMe); δ_C (67.8 MHz, $CDCl_3$) 165.7 (C=O), 165.5 (C=O), 144.4 (Ph*C*=C), 144.2 (Ph*C*=C), 136.0, 133.3, 130.8, 130.4, 126.6, 123.0, 118.8 (CO*C*=C), 118.6 (CO*C*=C), 100.1 (C1), 70.8 (C4, C2), 68.6 (C3), 59.6 (C5), 56.3 (Me); HRMS (ESI) Found: 602.9616 [M + Na]$^+$. Calc. for $C_{24}H_{22}O_7Br_2Na$ 602.9631.

Photoirradiation of compound 5 for 4 h. A solution of compound **5** (41 mg, 0.097 mmol) in $CHCl_3$ (4 mL), which was bubbled with argon gas prior to the reaction, was irradiated for 4 h at 16 °C with a 500 W Hg(Xe) lamp (band-filtered at 313 nm). After removal of the solvent, the residue was chromatographed on silica-gel (hexane–ethyl acetate, 5 : 2 to 2 : 1) to give the isomeric mixture of methyl β-D-xylopyranoside-2,4-truxinates (**7**; 3 mg, 7%) and three fractions (**Fr1**, **Fr2**, **Fr3**) each containing the mixture in different ratios of methyl 2-*O*-(*Z*)-cinnamoyl-4-*O*-(*E*)-cinnamoyl-β-D-xylopyranoside (**5**$_{Z,E}$; 21%), methyl 2-*O*-(*E*)-cinnamoyl-4-*O*-(*Z*)-cinnamoyl-β-D-xylopyranoside (**5**$_{E,Z}$; 21%), and methyl 2,4-di-*O*-(*Z*)-cinnamoyl-β-D-xylopyranoside (**5**$_{Z,Z}$; 26%).

Fr1 (6 mg) includes **5**$_{E,Z}$, **5**$_{Z,E}$, and **5**$_{Z,Z}$ in the ratio 0.13 : 0.361 : 0.51; $[a]_D^{22}$ −34.0 (*c* 0.75 in $CHCl_3$).

Fr2 (13 mg) includes **5**$_{E,Z}$, **5**$_{Z,E}$, and **5**$_{Z,Z}$ in the ratio 0.26 : 0.33 : 0.41; $[a]_D^{22}$ −42.6 (*c* 0.63 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$, H: **5**$_{Z,Z}$, H′: **5**$_{Z,E}$, H″: **5**$_{E,Z}$) 7.73 (0.26H, d, *J* 16.0, (*E*)–Ph*H*″C=C), 7.72 (0.34H, d, *J* 16.0, (*E*)–Ph*H*′C=C), 7.61–7.32 (10H, m, Ar), 7.03–6.96 (1.41H, m, (*Z*)–Ph*H*C=C, (*Z*)–Ph*H*′C=C, (*Z*)–Ph*H*″C=C), 6.43 (0.33H, d, *J* 16.0, (*E*)–CO*H*′C=C), 6.42 (0.26H, d, *J* 16.0, (*E*)–CO*H*″C=C), 6.01–5.94 (1.41H, m, (*Z*)–CO*H*C=C, (*E*)–CO*H*C=C, (*Z*)–CO*H*′C=C, (*Z*)–CO*H*″C=C), 4.95–4.83 (2H, m, 2-H, 2-H′, 2-H″, 4-H, 4-H′, 4-H″), 4.59 (0.26H, d, $J_{1,2}$ 4.4, 1-H″), 4.55 (0.33H, d, $J_{1,2}$ 4.7, 1-H′), 4.43 (0.41H, d, $J_{1,2}$ 5.2, 1-H), 4.20 (0.33H, dd, $J_{4,5a}$ 3.7, $J_{5a,5b}$ 12.7, 5-H′a), 4.17 (0.26H, dd, $J_{4,5a}$ 4.0, $J_{5a,5b}$ 12.8, 5-H″a), 4.12 (0.41H, dd, $J_{4,5a}$ 4.1, $J_{5a,5b}$ 12.4, 5-Ha), 3.91–3.87 (0.59H, m, 3-H′, 3-H″), 3.75 (0.41H, bq, 3-H), 3.56 (0.33H, dd, $J_{4,5b}$ 5.5, $J_{5a,5b}$ 12.7, 5-H′b), 3.52 (0.26H, dd, $J_{4,5b}$ 5.6, $J_{5a,5b}$ 12.8, 5-H″b), 3.49 (0.78H, s, OMe″), 3.48 (0.99H, s, OMe′), 3.45 (1.23H, s, OMe), 3.40 (0.41H, dd, $J_{4,5b}$ 6.4, $J_{5a,5b}$ 12.4, 5-Hb), 3.04 (0.33H, d, $J_{3,OH}$7.5, OH″), 3.01 (0.26H, d, $J_{3,OH}$ 7.5, OH′), 2.81 (0.41H, d, $J_{3,OH}$ 7.0, OH); δ_C (67.8 MHz, $CDCl_3$) 166.3 (C=O), 166.0 (C=O), 165.4 (C=O), 165.4 (C=O), 165.2 (C=O), 165.1 (C=O), 146.1, 145.9, 144.6, 144.5, 144.5, 134.6, 134.5, 134.5, 134.2, 130.5, 129.8, 129.7, 129.3, 129.3, 129.3, 128.9, 128.2, 128.1, 128.0, 118.9, 118.7, 118.6, 117.3, 117.2, 100.5 (C1), 100.4 (C1′), 100.2 (C1″), 71.3, 71.0, 70.9, 70.8, 70.8, 69.9 (C3), 69.4 (C3′), 69.3 (C3″), 60.4 (C5), 60.1 (C5′), 59.9 (C5″), 56.3 (Me); HRMS (ESI) Found: 447.1440 [M + Na]$^+$. Calc. for $C_{24}H_{24}O_7Na$ 447.1421.

Fr3 (15 mg) includes **5**, **5**$_{E,Z}$, **5**$_{Z,E}$, and **5**$_{Z,Z}$ in the ratio 0.47 : 0.24 : 0.15 : 0.14; $[a]_D^{22}$ −34.0 (*c* 0.75 in $CHCl_3$).

Photoirradiation of compound 5 for 44 h. A solution of compound **5** (30 mg, 0.071 mmol) in $CHCl_3$ (3 mL), which was bubbled with argon gas prior to the reaction, was irradiated for 44 h at 16 °C with a 500 W Hg(Xe) lamp (band-filtered at 313 nm). After removal of the solvent, the residue was chromatographed on silica-gel (toluene–ethyl acetate, 5 : 1) to give four fractions (**Fr1**, **Fr2**, **Fr3**, **Fr4**) each containing the isomeric mixture of methyl β-D-xylopyranoside-2,4-truxinates (**7**).

Fr1 (2 mg) includes a single isomer of methyl β-D-xylopyranoside-2,4-β-truxinate (**7B**) as a syrup; R_f 0.40 (hexane–ethyl acetate, 2 : 1); $[a]_D^{22}$ −44.3 (*c* 0.08 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.14–7.03 (6H, m, Ar), 6.93–6.88 (4H, m, Ar), 5.11 (1H, s, 1-H), 4.75–4.74 (1H, m, 2-H), 4.73–4.71 (1H, m, 4-H), 4.70–4.68 (2H, m, Ph*H*C=C × 2), 4.51–4.47 (1H, m, 3-H), 4.33 (1H, dd, $J_{4,5a}$ 1.5, $J_{5a,5b}$ 13.4, 5-Ha), 4.20–4.16 (1H, m, 5-Hb), 3.93–3.83 (2H, m, CO*H*C=C × 2), 3.86 (1H, d, $J_{3,OH}$ 10.1, OH), 3.56 (3H, s, OMe); δ_C (67.8 MHz, $CDCl_3$) 174.4 (C=O), 170.2 (C=O), 138.3, 128.1, 128.1, 128.0, 127.9, 127.8, 127.6, 126.5, 126.4, 98.7 (C1), 73.0 (C2), 71.8 (C4), 60.2 (C3), 56.7 (C5), 56.1 (Me), 46.5 (cyclobutane), 46.2 (cyclobutane), 43.3 (cyclobutane), 43.1 (cyclobutane); HRMS (ESI) Found: 447.1463 [M + Na]$^+$. Calc. for $C_{24}H_{24}O_7Na$ 447.1421.

Fr2 (3 mg) includes two methyl β-D-xylopyranoside-2,4-β-truxinates (**7A** and **7B**) in the ratio 0.74 : 0.26; $[a]_D^{22}$ −34.0 (*c* 0.15 in $CHCl_3$).

Fr3 (14 mg) includes another isomer of methyl β-D-xylopyranoside-2,4-β-truxinate (**7A**) as a syrup; R_f 0.36 (hexane–ethyl acetate, 2 : 1); $[a]_D^{22}$ −35.6 (*c* 0.70 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.13–7.06 (6H, m, Ar), 6.93–6.88 (4H, m, Ar), 4.93 (1H, d, $J_{1,2}$ 0.6, 1-H), 4.77–4.73 (2H, m, 2-H, 4-H), 4.58–4.47 (3H, m, 3-H, Ph*H*CC × 2), 4.31 (1H, dd, $J_{4,5a}$ 1.4, $J_{5a,5b}$ 13.3, 5-Ha), 4.19–4.08 (2H, m, CO*H*CC × 2), 3.91–3.85 (1H, m, 5-Hb), 3.81 (1H, d, $J_{3,OH}$ 9.9, OH), 3.54 (3H, s, OMe); δ_C (67.8 MHz, $CDCl_3$) 171.7 (C=O), 171.4 (C=O), 138.3, 129.0, 128.7, 128.2, 127.8, 126.6, 126.3, 98.9 (C1), 71.8 (C2), 69.4 (C4), 59.3 (C3), 57.0 (C5), 56.1 (Me), 45.0 (cyclobutane), 44.9 (cyclobutane), 42.3 (cyclobutane); HRMS (ESI) Found: 447.1422 [M + Na]$^+$. Calc. for $C_{24}H_{24}O_7Na$ 447.1421.

Fr4 (7 mg) includes methyl β-D-xylopyranoside-2,4-β-truxinate (**7A**), methyl β-D-xylopyranoside-2,4-δ-truxinate (**7C**), and methyl β-D-xylopyranoside-2,4-ξ-truxinate (**7D**), in the ratio 0.48 : 0.29 : 0.23; $[a]_D^{22}$ −31.7 (*c* 0.36 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$, H: **7A**, H′: **7C**, H″: **7D**) COSY δ 7.37–6.88 (10H, m, Ar), 4.93 (0.48H, s, 1-H), 4.87 (0.29H, s, 1-H′), 4.85 (0.23H, s, 1-H″), 4.77–4.73 (1.48H, m, 2-H, 4-H, 2-H′, 4-H″), 4.73–4.64 (0.58H, m, Ph*H*′CC × 2), 4.58–4.46 (1.94H, m, 3-H, Ph*H*CC, 3-H′, 3-H″, 2-H″, 4-H″), 4.33–4.21 (1H, m, 5-Ha, 5-H′a, 5-H″a), 4.19–4.08 (0.94H, m, Ph*H*CC, Ph*H*″CC × 2), 4.04–3.97 (0.58H, m, CO*H*′CC × 2), 3.91–3.82 (0.77H, m, 5-Hb, 5-H′b), 3.82–3.69 (2.42H, m, OH, OH′, 5-H″b, CO*H*CC × 2, CO*H*″CC × 2), 3.60 (0.23H, d, $J_{3,OH}$ 9.6, OH″), 3.54 (1.44H, s, OMe), 3.51 (1.56H, s, OMe′, OMe″); δ_C (67.8 MHz, $CDCl_3$) 171.4, 171.3, 171.0, 141.4, 138.7, 138.3, 129.0, 128.7, 128.2, 128.0, 127.8, 127.0, 126.7, 126.6, 126.3, 99.1, 98.9, 98.7, 71.8, 71.6, 69.4, 69.3, 59.3, 58.8, 58.6, 57.2, 57.0, 56.9, 56.1, 56.0, 46.8, 46.6,

45.7, 45.5, 45.0, 44.9, 44.1, 44.0, 42.3, 41.8, 29.7; HRMS (ESI) Found: 425.1640 $[M + H]^+$. Calc. for $C_{24}H_{25}O_7$ 425.1601.

Ester exchange reaction for methyl β-D-xylopyranoside-2,4-truxinates. A mixture of methyl β-D-xylopyranoside-2,4-β-truxinates (**7**: 24 mg, 0.056 mmol) in **Fr1**, **Fr2**, **Fr3** obtained in the previous section were treated with $SOCl_2$–MeOH (1 : 100, 5.0 mL) under argon gas for 3 days at room temperature. After evaporation, the mixture was dissolved in $CHCl_3$, washed with sat. $NaHCO_3$, dried over $MgSO_4$, and evaporated to give β-truxinate **8**β (15.5 mg, 85%) as a white solid: δ_H (400 MHz, $CDCl_3$) 7.12–6.89 (10H, m, Ar), 4.41–4.39 (2H, m, Ph*H*CC × 2), 3.86–3.84 (2H, m, CO*H*CC × 2), 3.75 (6H, s, OMe); δ_C (67.8 MHz, $CDCl_3$) 172.9 (C=O), 138.4, 128.0, 127.7, 126.4, 52.2 (Me), 44.9 (cyclobutane), 43.2 (cyclobutane); HRMS (ESI) Found: 347.1264 $[M + Na]^+$. Calc. for $C_{20}H_{20}O_4Na$ 347.1260.

A mixture of β-truxinate **8**β, δ-truxinate **8**δ, and ξ-truxinate **8**ξ (0.7 : 0.2 : 0.1) was obtained through the above treatment from **Fr4**: δ_H (400 MHz, $CDCl_3$) 7.36–6.92 (10H, m, Ar), 4.66 (0.1H, t, *J* 10.4, ξ-Ph*H*CC), 4.38–4.36 (1.4H, m, β-Ph*H*CC × 2), 3.96–3.84 (0.2H, m, ξ-Ph*H*CC, ξ-CO*H*CC), 3.83–3.81 (1.4H, m, β-CO*H*CC × 2), 3.78 (0.6H, s, δ-OMe), 3.72 (4.2H, s, β-OMe × 2), 3.70 (0.3H, s, ξ-OMe), 3.73–3.68 (1.0H, m, δ-Ph*H*CC × 2, δ-OMe), 3.47 (0.4H, m, δ-CO*H*CC × 2), 3.35–3.31 (0.1H, m, ξ-CO*H*CC), 3.27 (0.3H, s, ξ-OMe); δ_C (67.8 MHz, $CDCl_3$) 172.9, 138.4, 128.9, 128.6, 128.5, 128.3, 128.1, 127.9, 127.7, 127.3, 127.12, 127.07, 126.8, 126.6, 125.4, 52.1, 51.9, 47.3, 46.8, 44.9, 44.6, 44.4, 43,3, 43.2, 29.7; HRMS (ESI) Found: 347.1264 $[M + Na]^+$. Calc. for $C_{20}H_{20}O_4Na$ 347.1260.

Photoirradiation of compound 5d_{14} for 44 h. A solution of compound **5**d_{14} (47 mg, 0.107 mmol) in $CHCl_3$ (5 mL), bubbled with argon gas prior to the reaction, was irradiated for 44 h at 16 °C with a 500 W Hg(Xe) lamp (band-filtered at 313 nm). After removal of the solvent, the residue was chromatographed on silica-gel (toluene–ethyl acetate, 5 : 1) to give both isomers of methyl β-D-xylopyranoside-2,4-β-truxinates-d_{14} **7**d_{14}A (15 mg, 32%) and **7**d_{14}B (5 mg, 11%) as syrups and a fraction (**Fr3**; 15 mg, 32%) containing the mixture of methyl β-D-xylopyranoside-2,4-truxinates-d_{14} (**7**d_{14}).

*7*d_{14}*A*. $[\alpha]_D^{22}$ −37.9 (*c* 0.77 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 4.93 (1H, s, 1-H), 4.77–4.74 (1H, m, 2-H, 4-H), 4.57–4.53 (1H, m, 3-H), 4.31 (1H, d, $J_{5a,5b}$ 13.4, 5-Ha), 3.89 (1H, d, $J_{5a,5b}$ 13.4, 5-Hb), 3.81 (1H, d, $J_{3,OH}$ 9.8, OH), 3.55 (3H, s, OMe); δ_C (67.8 MHz, $CDCl_3$) 171.7 (C=O), 171.4 (C=O), 138.1, 127.8, 127.5, 127.1, 98.9 (C1), 71.8 (C2), 69.4 (C4), 59.2 (C3), 57.0 (C5), 56.1 (Me), 29.7 (m, cyclobutane); HRMS (ESI) Found: 461.2286 $[M + Na]^+$. Calc. for $C_{24}H_{10}D_{14}O_7Na$ 461.2298.

*7*d_{14}*B*. $[\alpha]_D^{22}$ −65.0 (*c* 0.14 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 5.07 (1H, s, 1-H), 4.72–4.70 (1H, m, 2-H), 4.70–4.69 (1H, m, 4-H), 4.47–4.42 (1H, m, 3-H), 4.29 (1H, dd, $J_{4,5a}$ 1.2, $J_{5a,5b}$ 13.4, 5-Ha), 3.83 (1H, d, $J_{5a,5b}$ 13.4, 5-Hb), 3.83 (1H, d, $J_{3,OH}$ 9.9, OH), 3.53 (3H, s, OMe); δ_C (67.8 MHz, $CDCl_3$) 174.4 (C=O), 170.2 (C=O), 98.7 (C1), 73.0 (C2), 69.9 (C4), 60.2 (C3), 56.7 (C5), 56.1 (Me); HRMS (ESI) Found: 461.2296 $[M + Na]^+$. Calc. for $C_{24}H_{10}D_{14}O_7Na$ 461.2298.

Fr3 includes methyl β-D-xylopyranoside-2,4-β-truxinate-d_{14} (**7**d_{14}A), methyl β-D-xylopyranoside-2,4-δ-truxinate-d_{14} (**7**d_{14}C), and methyl β-D-xylopyranoside-2,4-ξ-truxinate-d_{14} (**7**d_{14}D), in the ratio 0.5 : 0.25 : 0.25; $[\alpha]_D^{22}$ −38.0 (*c* 0.76 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$, H: **7**d_{14}A, H′: **7**d_{14}C, H″: **7**d_{14}D) 4.90 (0.5H, s, 1-H), 4.84 (0.25H, s, 1-H′), 4.82 (0.25H, s, 1-H″), 4.74–4.70 (1.5H, m, 2-H, 2-H′, 4-H, 4-H″), 4.54–4.42 (1.5H, m, 3-H, 3-H′, 3-H″, 2-H″, 4-H″), 4.29–4.18 (1H, m, 5-Ha, 5-H′a, 5-H″a), 3.87–3.73 (1.75H, m, 5-Hb, 5-H′b, OH, OH′, 5-H″b), 3.58 (0.25H, d, $J_{3,OH}$ 9.6, OH″), 3.51 (1.5H, s, OMe), 3.47 (1.5H, s, OMe′, OMe″); δ_C (67.8 MHz, $CDCl_3$) 171.7, 171.4, 171.3, 170.9, 170.5, 141.1, 139.9, 139.7, 138.5, 138.4, 127.8, 127.7, 127.4, 127.1, 126.1, 125.8, 99.1 (C1), 98.9 (C1), 98.7 (C1), 71.8, 71.6, 69.4, 69.3, 59.2, 58.8, 58.6, 57.2, 57.0, 56.9, 56.1, 56.0, 29.7; HRMS (ESI) Found: 461.2286 $[M + Na]^+$. Calc. for $C_{24}H_{10}D_{14}O_7Na$ 461.2298.

Photoirradiation of compound 5Br for 44 h. A solution of compound **5Br** (46 mg, 0.079 mmol) in $CHCl_3$ (3.5 mL), bubbled with argon gas prior to the reaction, was irradiated for 44 h at 16 °C with a 500 W Hg(Xe) lamp (band-filtered at 313 nm). After removal of the solvent, the residue was chromatographed on silica-gel (hexane–ethyl acetate, 2 : 1 to 3 : 2) to give a fraction (**Fr1**) containing the isomeric mixture of methyl β-D-xylopyranoside-2,4-β-3,3′-dibromotruxinates (**7BrA** and **7BrB**; 11 mg, 24%) and a single isomer of methyl β-D-xylopyranoside-2,4-β-3,3′-dibromotruxinate **7BrA** (20 mg, 43%) as a syrup.

7BrA. R_f 0.20 (hexane–ethyl acetate, 3 : 2); $[\alpha]_D^{22}$ −35.2 (*c* 1.00 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.26–6.78 (8H, m, Ar), 4.93 (1H, s, 1-H), 4.76–4.72 (2H, m, 2-H, 4-H), 4.40–4.56 (3H, m, 3-H, Ph*H*CC × 2), 4.30 (1H, d, $J_{5a,5b}$ 13.3, 5-Ha), 4.05–4.13 (2H, m, CO*H*CC × 2), 3.89 (1H, d, $J_{5a,5b}$ 13.3 Hz, 5-Hb), 3.82 (1H, d, $J_{3,OH}$ 9.5, OH), 3.55 (3H, s, OMe); δ_C (67.8 MHz, $CDCl_3$) 171.2 (C=O), 170.9 (C=O), 140.2, 130.8, 130.75, 129.8, 129.75, 129.69, 129.67, 126.51, 126.47, 122.4, 98.8 (C1), 72.0 (C2), 69.5 (C4), 59.2 (C3), 57.0 (C5), 56.1 (Me), 44.6 (cyclobutane), 44.5 (cyclobutane), 42.0 (cyclobutane), 42.0 (cyclobutane); HRMS (ESI) Found: 580.9770 $[M + H]^+$. Calcd for $C_{24}H_{23}O_7Br_2$ 580.9811.

Fr1 includes **7BrA** and methyl β-D-xylopyranoside-2,4-β-3,3′-dibromotruxinate (**7BrB**), in the ratio 0.83 : 0.17; R_f 0.20 (hexane–ethyl acetate, 3 : 2); $[\alpha]_D^{22}$ −36.6 (*c* 0.56 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.26–6.78 (8H, m, Ar), 5.11 (0.17H, s, 1-H′), 4.92 (0.83H, s, 1-H), 4.78–4.72 (2H, m, 2-H, 2-H′, 4-H, 4-H′), 4.64–4.61 (0.34H, m, Ph*H*′CC × 2), 4.54–4.41 (2.66 H, m, 3-H, 3-H′, Ph*H*CC × 2), 4.33–4.27 (1H, m, 5-Ha, 5-H′a), 4.16 (0.17H, d, $J_{5a,5b}$ 13.8, 5-H′b), 4.13–4.02 (1.66H, m, CO*H*CC × 2), 3.90–3.79 (2.17H, m, 5-Hb, CO*H*′CC × 2, OH, OH′), 3.56 (0.51H, s, OMe′), 3.55 (2.49H, s, OMe); δ_C (67.8 MHz, $CDCl_3$) 171.2 (C=O), 170.9 (C=O), 170.0 (C=O), 130.8, 130.8, 130.8, 130.8, 129.9, 129.8, 129.7, 129.7, 129.7, 126.5, 126.5, 126.3, 126.1, 122.5, 122.4, 122.4, 98.8 (C1), 98.7 (C1′), 73.2 (C2′), 72.0 (C2), 70.0 (C4′), 69.5 (C4), 60.2 (C3′), 59.2 (C3), 57.0 (C5), 56.6 (C5′), 56.1 (Me), 56.1 (Me′), 46.1 (cyclobutane′), 42.8 (cyclobutane′), 42.0 (cyclobutane), 42.0 (cyclobutane); HRMS (ESI) Found: 580.9818 $[M + H]^+$. Calcd for $C_{24}H_{23}O_7Br_2$ 580.9811.

Ester exchange reaction for methyl β-D-xylopyranoside-2,4-β-3,3′-dibromotruxinates (7Br). A mixture of methyl β-D-xylopyranoside-2,4-β-3-bromotruxinates (**7Br**: 65 mg, 0.112 mmol) in **Fr1** obtained in the previous section were treated with $SOCl_2$–MeOH (1 : 100, 5.0 mL) under argon gas for 15 h at room temperature. After evaporation, the mixture was dissolved in $CHCl_3$, washed with sat. $NaHCO_3$, dried over $MgSO_4$, and evaporated. The residue was chromatographed on silica-gel (hexane–ethyl acetate, 2 : 1 to 3 : 2) to give β-3,3′-dibromotruxinate **8Br**β (52 mg,

97%) as a white solid: δ_H (400 MHz, $CDCl_3$) 7.22 (1H, m, 4-H–Ph), 7.09 (1H, t, *J* 1.6, 2-H–Ph), 7.00 (1H, t, *J* 7.9, 5-H–Ph), 6.81 (1H, m, 6-H–Ph), 4.35, 3.72 (2H, each m, cyclobutane), 3.76 (6H, s, OMe × 2); δ_C (67.8 MHz, $CDCl_3$) 172.4, 140.3, 130.7, 129.8, 129.7, 126.4, 122.3, 52.3, 44.5, 42.9; HRMS (ESI) Found: 502.9497 $[M + Na]^+$. Calc. for $C_{20}H_{18}O_4Br_2Na$ 502.9470.

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