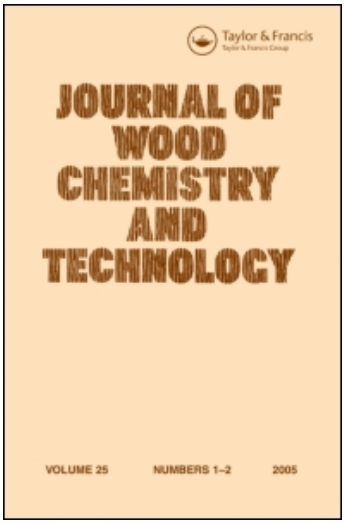

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ABSTRACT

A novel degradation method of arylglycerol-β-aryl (β-*O*-4) ether substructure in lignins without any secondary condensation reactions named TIZ method was developed. The TIZ method consists of three reaction steps: (1) selective tosylation (T) of primary hydroxyl group, (2) iodination (I), and (3) zinc-metal treatment (Z) to cleave of β-*O*-4 linkage. This method was applied to two nonphenolic β-*O*-4 lignin substructure compounds of guaiacyl and syringyl type: benzylguaiacylglycerol-β-guaiacyl ether (**1a**) and benzylsyringylglycerol-β-syringyl ether (**1b**). Respective reaction steps were performed quantitatively concerning both guaiacyl and syringyl models.

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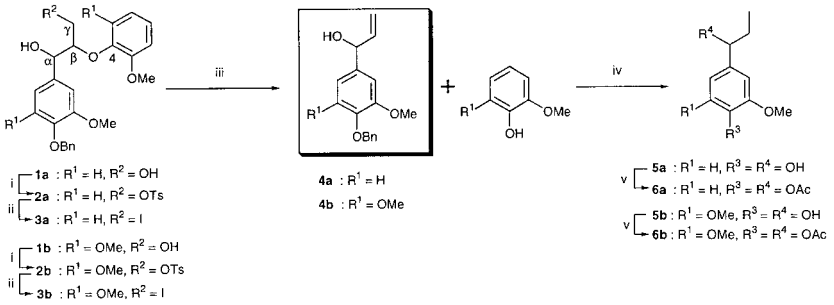
After zinc treatment, almost 1 mole of olefinic compounds, 3-benzyl-guaiacyl-3-hydroxy-1-propene (**4a**) and 3-benzylsyringyl-3-hydroxy-1-propene (**4b**), were formed from 1 mol of compound **1a** and **1b**, respectively. This indicates that β-*O*-4 linkage in compound **1a** and **1b** was cleaved quantitatively without formation of any by-products. The structures of the degradation products from compound **1a** and **1b** by TIZ method were determined by ^{1}H and ^{13}C NMR spectroscopy and GC–MS, and by comparison with authentic compounds synthesized independently. The degradation products were quantified by GC. The TIZ method, carried out under weak alkaline and neutral reaction conditions, was shown to be useful for the selective cleavage of β-*O*-4 linkage of compound **1a** and **1b** without secondary condensation reaction on side chain. Therefore, this method is an efficient analytical method for lignin structure studies.

INTRODUCTION

Lignin is one of the main components of wood cell walls same as cellulose and hemicellulose. Differently from other natural polymer such as protein and polysaccharide, lignin is a structuraly irregular polymer consisting of phenylpropane units, linked by carbon–carbon linkage and ether linkage at random. Therefore, for structural studies of lignins, degradation of lignin polymer to low molecular weight compounds, which could be reconstructed to the structures of the original lignins, has been applied.

The β-*O*-4 substructure is the most important substructure in lignins.[1,2] Several degradation methods such as acidolysis,[3] thioacidolysis[4,5] and DFRC[6,7] method, have been applied for the substructure and contributed for the construction of the structural scheme of lignins. However, it has been known that acidolysis which is conducted under acidic conditions gives many by-products via secondary condensation even from the β-*O*-4 substructure compounds. In thioacidolysis, secondary condensation can be avoided to some degree because benzyl cation at C-α position is inactivated by nucleophilic attack of ethanthiol, but the use of BF_3–Et_2O is acidic.[4] Currently, DFRC method has been applied for analysis of lignins because of its high structure selectivity. But acetyl bromide solution utilized in the DFRC method is strong acid. Thus, there remain some possibilities of unexpected secondary condensations in acidolysis, thioacidolysis and also DFRC method, because all of them are performed under acid conditions. In addition, the information about α-position postulated structure in lignin–carbohydrate complex[8,9] are not obtained by such conventional degradation methods for β-*O*-4



Scheme 1. The degradation of β-*O*-4 model compounds by TIZ method: (i) TsCl, Py, r.t., 6.5 h; (ii) KI, DMF, 100°C, 5 h; (iii) Zn, dioxane–H_2O (9:1 v/v), 50°C, 2 h; (iv) H_2, Pd–C (10%), dioxane–H_2O (9:1 v/v), r.t., 1 h; (v) Ac_2O–Py (1:1 v/v), 60°C, 1 h.

substructure carried out under acidic conditions because the native structure on α-position is lost.

Then, a new degradation method, which is performed under neutral conditions, is needed to avoid any secondary reaction. Thus, a novel degradation method of β-*O*-4 substructure in lignins, named TIZ method, has been developed[10] (Sch. 1). This method is conducted under weak alkaline (in pyridine) and neutral conditions. Therefore, in the TIZ method, secondary condensation reactions may not occur and both the degradation products and the residual products may retain the native lignin structures. In this article, it is demonstrated that TIZ method can degrade β-aryl ether bond in representative lignin model compounds, quantitatively.

RESULTS AND DISCUSSION

Strategy

Generally, ether linkages are stable and degraded only under strong acid reaction conditions. However, Boord reported in 1931 that ether bond such as β-halogenoether is cleaved reductively with zinc metal to give olefinic compound and alcohol.[11] For applying this type of reaction to the β-*O*-4 structures in lignin, the primary hydroxyl groups at γ-positions have to be converted to halogen atoms.

On the other hand, the iodination method of lignin molecules has been reported already by Freudenberg to determine primary hydroxyl

contents;[12] the substitution tosyl group (*p*-toluenesulfonyl) for the γ-hydroxyl group and subsequent iodination. However, the reductive cleavage of the β-*O*-4 structures in lignin by reaction of β-halogenoether in lignin with zinc dust has not yet been conducted. Then, a series of the TIZ reaction, tosylation, halogenation, and subsequent reductive cleavage of the β-*O*-4 structures of lignin model compounds were attempted.

Tosylation

According to Freudenberg's method, tosylation was conducted with tosyl chloride (4.0 equiv.) at 3°C for 48 h. But under these conditions, the primary hydroxyl group in compound **1a** was not tosylated quantitatively and required more time. Thus, the reaction condition of tosylation was modified to obtain optimum reaction condition for selective tosylation of the primary hydroxyl group.

Both the guaiacyl type model compound **1a** (erythro and threo isomers mixture) and the syringyl type model compound **1b** (erythro isomer), were tosylated quantitatively with tosyl chloride (5.0 equiv.) in pyridine at room temperature for 6 h. The ^{1}H NMR spectra of tosylates, **2a** and **2b**, were shown in Figs. 1(B) and 2(B), respectively. The methyl and aromatic signals of tosyl group appeared at 2.4 ppm and at 7.21 ~ 7.28, 7.63 ~ 7.70 ppm, respectively, and γ-protons signals of compound **1a** (erythro and threo mixture) were shifted largely toward downfield (from 2.88 ~ 3.00, 3.43 ~ 3.69 ppm to 3.90 ~ 4.31 ppm). This indicates that only the primary hydroxyl group at the γ-position was completely tosylated to give compound **2a** or **2b**. The tosylation can be followed by the increase of the methyl proton signal of the tosyl group on the ^{1}H NMR spectrum as shown in Fig. 3. The yields of compound **2a** and **2b** were calculated by the ratio of the peak area of the methyl group in the tosyl group against that of the methylene group in the benzyl group: [Area-CH_3 of the tosyl group/Area-CH_2 of the benzyl group]. The tosylation was complete in 3 h for the guaiacyl (**1a**) and 6 h for the syringyl compound (**1b**). The difference in reaction times may be caused by the steric hindrance of the additional methoxyl group in **1b**. The reactivities of erythro and threo isomers of compound **1a** were almost same.

Iodination

According to Freudenberg's method, iodination was conducted with sodium iodide (2.4 equiv.) in acetone at room temperature for 50 h.

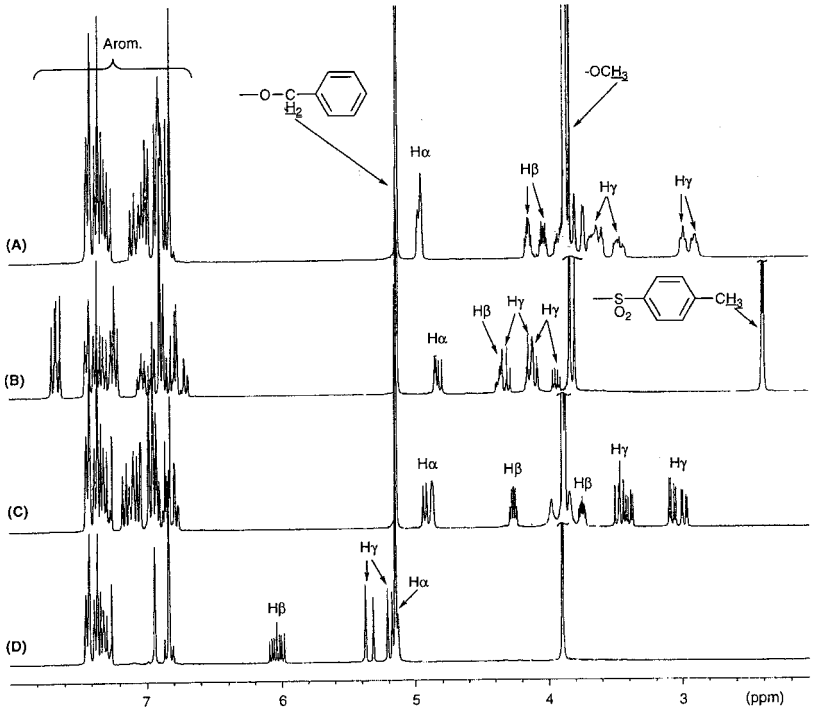


Figure 1. ^{1}H-NMR spectra of each derivative, tosylate (**2a**): B, iodinate (**3a**): C, and terminal olefine (**4a**): D from compound **1a**: A.

But too much time was needed under these conditions. Thus, the reaction conditions of iodination were modified.

The guaiacyl (**2a**) and syringyl tosylate (**2b**) were iodinated quantitatively with potassium iodide (5.0 equiv.) in dry DMF at 100°C for 5 h. The ^{1}H NMR spectra of the iodinates (**3a** and **3b**) are shown in Figs. 1(C) and 2(C), respectively. The methyl signals (at 2.4 ppm) and aromatic signals (at 7.21 ~ 7.28, 7.63 ~ 7.70 ppm) of the tosyl group disappeared after iodination, and the γ-protons signals of **2a** (erythro and threo mixture) were shifted upfield (from 3.93–4.31 ppm to 3.07–3.47 ppm). In addition, the typical ^{13}C NMR carbon signals of the γ-methylene of **3a** and **3b** appeared at 3.8 ppm for the guaiacyl and 2.3 ppm for the syringyl respectively. This indicates that the tosyl group was substituted for iodine to give compound **3a** and **3b**. The iodination can be followed by the decrease of the methyl proton signals of the tosyl group in the ^{1}H NMR spectrum as shown in Fig. 4. The yields of compound **3a** and **3b**

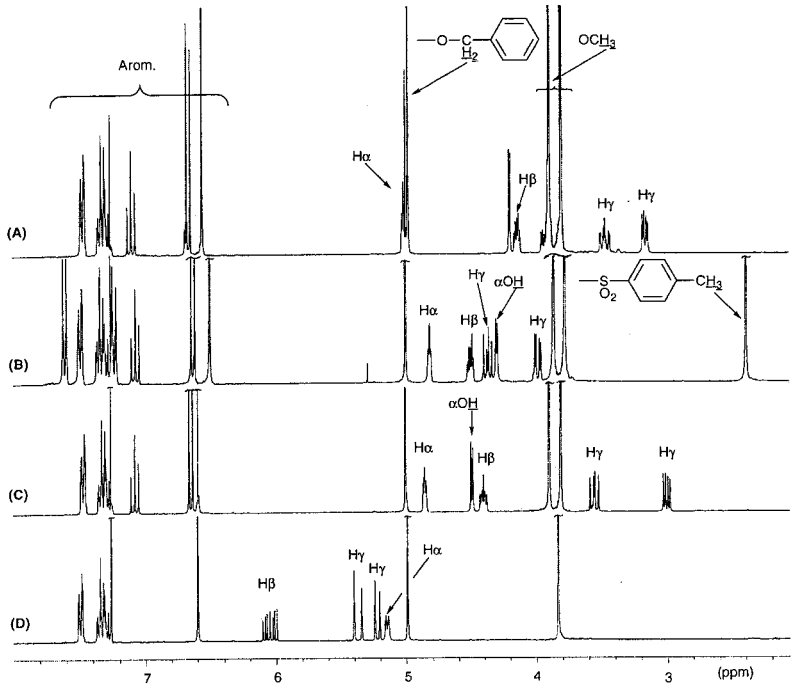


Figure 2. ^{1}H-NMR spectra of each derivative, tosylate (**2b**): B, iodinate (**3b**): C, and terminal olefine (**4b**): D from compound **1b**: A.

were calculated by the ratio of the peak area of the methyl group in the tosyl group against that of the methylene group in the benzyl group: [Area-CH_3 of the tosyl group/Area-CH_2 of the benzyl group]. The detosylation and the following iodination was complete in 1 h for the guaiacyl (**2a**) and 5 h for the syringyl compound (**2b**). The difference in reaction times may also be caused by the steric hindrance of the additional methoxyl group of **2b** as in the tosylation. There was not much difference between potassium iodine and sodium iodine as a resource of iodine ion. The reactivities of erythro and threo isomers of compound **2a** were almost same.

Zinc Treatment

In Boord's method, the zinc treatment is carried out with zinc metal and zinc chloride in 1-butanol. Zinc chloride is used to activate the zinc

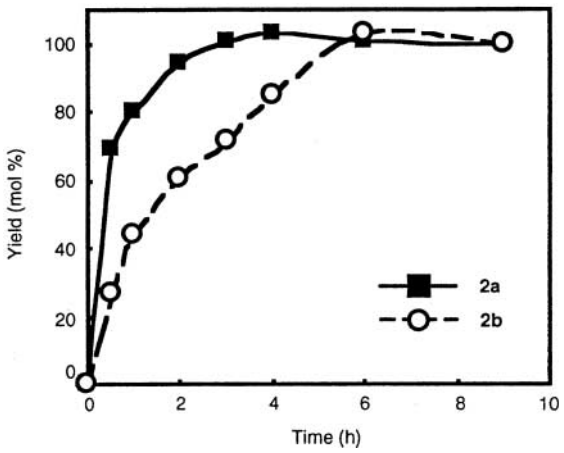


Figure 3. The yields of guaiacyl compound **2a** and syringyl compound **2b** in tosylation.

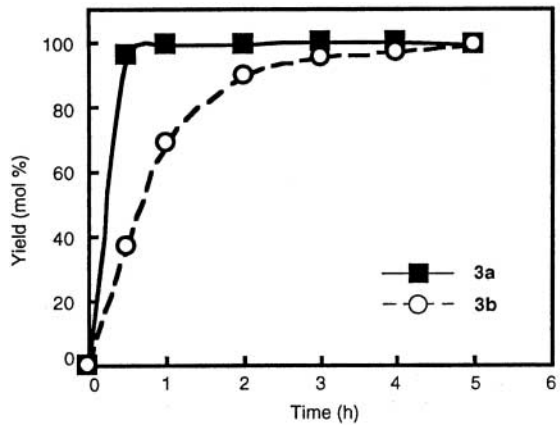


Figure 4. The yields of guaiacyl compound **3a** and syringyl compound **3b** in iodination.

metal, but it also acts as a Lewis acid in reaction solution. However, when the reductive reaction of Boord's method is applied to iodinated lignin model compounds (**3a** and **3b**), the expected olefinic reaction products are unstable because they both have α-hydroxyl group activated by both aryl and vinyl groups. Therefore, this reaction has to be conducted under

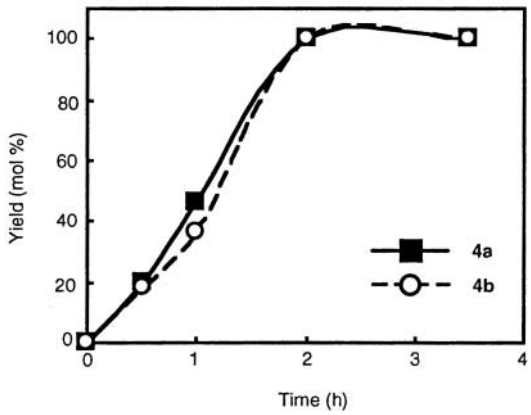


Figure 5. The yields of guaiacyl olefinic compound **4a** and syringyl olefinic compound **4b** in zinc treatment.

completely neutral conditions. Thus, the zinc metal dust previously activated by hydrochloric acid was used for zinc treatment.[13] Dioxane–H_2O (9:1, v/v) was selected as reaction solvent, because it is suitable solvent for most lignin samples.

The iodinated derivatives (**3a** and **3b**) were treated with activated zinc dust in dioxane–H_2O (9:1, v/v) at 50°C for 2 h. Zinc treatment of **3a** was quantitatively proceeded to give guaiacol and compound **4a**. The ^{1}H NMR spectrum of **4a** was shown in Fig. 1(D). The γ-proton signals of **3a** (erythro and threo mixture) disappeared after zinc treatment. The olefinic β-proton signal appeared at 6.03 ppm as a multiplet. Thus, the zinc treatment can be followed by the increase of the β-olefinic proton signal on the ^{1}H NMR spectrum as shown in Fig. 5. The yields of compound **4a** and **4b** were calculated by the ratio of the peak area of the β-olefinic proton of **4a** against the peak areas of both the β-olefinic proton of **4a** and the γ-proton of the iodinated derivative (**3a**): [Area-Hβ of **4a**/(Area-Hβ of **4a** + Area-Hγ of **3a**)]. The zinc treatment was finished in 2 h for both the guaiacyl and syringyl type. The reactivities of erythro and threo isomers of compound **3a** were almost the same. Likewise, compound **3b** was converted to syringol and compound **4b** after zinc treatment. The ^{1}H NMR spectrum of compound **4b** is shown in Fig. 2(D). Thus, it is demonstrated that the β-*O*-4 ether bond in guaiacyl and syringyl models is quantitatively cleaved without any side reactions by the zinc treatment of γ-iodinated derivatives.

Mechanism

The TIZ reaction sequence was applied to phenylcoumaran and β-1 model compounds to investigate the reactivities of other lignin substructures in lignin. Tosylation and subsequent iodination proceeded quantitatively. However, both iodides were recovered without any conversion after zinc-treatment. The result suggested that the β-haloether bond cleavage proceeds via a five members ring intermediate containing oxygen, zinc and iodine as shown in Fig. 6.

GC Analysis

Terminal olefin derivatives derived from iodinated derivatives (**3a** and 3**b**) seem to be structurally unstable. It is necessary to make the olefinic derivatives stable for their quantitative determination. Therefore, the olefinic derivatives were saturated by a catalytic hydrogenation. Hydrogenation of compounds **4a** and **4b** was finished in 1 h to quantitatively afford compounds **5a** and **5b**, respectively. Subsequently, compounds **5a** and **5b** were acetylated for analyses by GC. Compounds **6a** and **6b** were identified by comparison with authentic samples which were synthesized from vanillin and syringaldehyde. Figure 7 shows the gas chromatograms of the TIZ degradation products, 1-guaiacyl-1-propanol diacetate (**6a**) and 1-syringyl-1-propanol diacetate (**6b**), respectively. The relative simplicity in the resulting monomer composition makes quantitative analysis easy and accurate.

Thus, it is demonstrated that the presently developed TIZ method is very useful to degrade only the ether bond in β-*O*-4 structures with high structure selectivity without any secondary condensation reactions. The TIZ method is extremely important for the structure determination of the total lignin and for the open the new door of the future lignin chemistry.

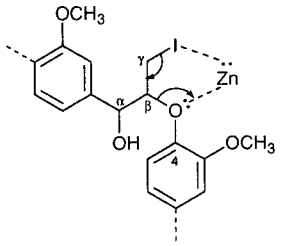


Figure 6. Reaction mechanism of the TIZ method.

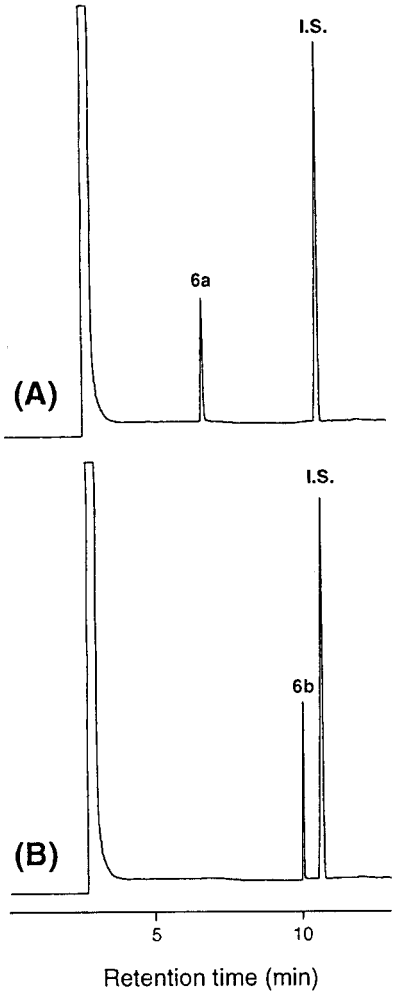


Figure 7. The gas chromatograms of TIZ monomers from compound **1a**: **A**, compound **1b**: B.

CONCLUSIONS

A novel cleavage method for arylglycerol-β-aryl ether bond in lignin, named TIZ method, was developed. This method consists of three steps; selective tosylation (T) of primary hydroxyl group at γ-position, iodination (I) and zinc reductive cleavage (Z). Lignin β-*O*-4 model

compounds **1a** and **1b** are quantitatively cleaved by TIZ method to afford compound **4a** and guaiacol, and compound **4b** and syringol, respectively. On the other hand, the phenylcoumaran and β-1 structure, without β-*O*-4 functional groups, can not be degraded by the TIZ method. Thus, it is demonstrated that the TIZ method is an excellent and useful method to degrade only the ether bond in β-*O*-4 structures with high structure selectivity and without any secondary condensation reactions.

EXPERIMENTAL

General

Anhydrous diethyl ether was distilled from NaH. Preparative thin layer chromatography (PTLC) was performed on silica gel plates (Kieselgel 60 F_{254}, Merck, 2 mm × 20 cm × 20 cm). The standard workup procedure included diluting with ethyl acetate, washing with water and brine, drying over Na_2SO_4, and concentration in vacuo.

Measurements

^1H and ^{13}C NMR spectra were collected with Varian INOVA300 FT-NMR (300 MHz) spectrometer, in chloroform-*d* with tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and coupling constants (J) were given in δ values (ppm) and Hz, respectively.

Gas chromatography (Shimadzu GC18A, Kyoto, Japan) with a flame ionization detector (FID) and a fused silica capillary column (Shimadzu OV18A, 30 m × 0.25 mm i.d., coated with 0.25 μm of 50%-phenyl-methylpolysiloxane, Kyoto, Japan) was used; column temperature: 230°C, injector temperature: 270°C, detector temperature: 270°C, and carrier gas: He (0.1 MPa). The identification of the peaks on the chromatogram was carried out using GC–MS (SHIMADZU QP5000, Kyoto, Japan) with an electron impact ionization source (70 eV). For quantitative determination, response factors of 0.4145 and 0.4816 for 1-guaiacyl-1-propanol diacetate (**6a**) and 1-syringyl-1-propane diacetate (**6b**), respectively, were used. The response factors were determined using the corresponding authentic compounds and *n*-tetracosane as an internal standard. The retention times of **6a**, **6b** , and *n*-tetracosane were 6.56, 10.02, and 10.34 min.

Materials and Reagents

Two nonphenolic lignin model compounds, 4-*O*-benzyl-guaiacyl-glycerol-β-guaiacyl ether (**1a**, erythro and threo isomers mixture) and 4-*O*-benzyl-syringylglycerol-β-syringyl ether (**1b**, erythro isomers) were synthesized according to the methods described in literature.[14,15]

p-Toluenesulfonyl chloride (tosyl chloride), pyridine, potassium iodide, dimethylformamide (DMF), zinc dust, dioxane were purchased from Nacalai Tesque Co. and ethylmagnesium bromide from Tokyo Kasei Kogyo Co., Ltd. All chemicals used were reagent grade and used without further purification. The activated zinc metal was prepared by treating with 5% HCl solution and subsequent successive washing with distilled water and acetone until the washings became neutral and then stocked in acetone.[16]

Tosylation of 4-*O*-Benzyl-guaiacylglycerol-β-guaiacyl Ether (**1a**)

4-*O*-Benzyl-guaiacylglycerol-β-guaiacyl ether (**1a**) (111.8 mg, 0.273 mM) was dissolved in 4 mL of dry pyridine, and then tosyl chloride (259 mg, 1.36 mM) was added. The reaction solution was kept at room temperature for 3 h, and worked-up by the standard method to afford colorless syrup, which was purified by PTLC developed with ethyl acetate–*n*-hexane (1:2, v/v) to give compound **2a** as a colorless syrup (149.9 mg, 98% yield), which gave two spots of erythro and threo isomers (1:1, m/m). ^{1}H NMR δ ($CDCl_3$) of erythro isomer: 2.40 (3H, s, C$H_3C_6H_4$), 3.67 (H, d, *J* 3.6, αOH), 3.83 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.07 (H, dd, *J* 10.2, 2.1, Hγ), 4.31 (H, dd, *J* 17.7, 7.5, Hγ), 4.38 (H, m, Hβ), 4.84 (H, t, *J* 3.6, Hα), 5.14 (2H, s, C$H_2C_6H_5$), 6.68–7.66 (12H, m, aromatic H), 7.23 (2H, d, *J* 8.1, aromatic H of tosyl group), 7.64 (2H, d, *J* 8.1, aromatic H of tosyl group), threo isomer: 2.42 (3H, s, C$H_3C_6H_4$), 3.85 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 3.93 (H, dd, *J* 12.0, 5.7, Hγ), 4.09 (H, s, αOH), 4.10 (H, m, Hβ), 4.12 (H, dd, *J* 12.0, 2.7, Hγ), 4.80 (H, d, *J* 7.8, Hα), 5.14 (2H, s, C$H_2C_6H_5$), 6.74–7.44 (12H, m, aromatic H), 7.26 (2H, d, *J* 8.1, aromatic H of tosyl group), 7.69 (2H, d, *J* 8.1, aromatic H of tosyl group); ^{13}C NMR δ ($CDCl_3$) of erythro isomer: 21.6 ($H_3CC_6H_4$), 55.9 (OCH_3), 55.7 (OCH_3), 68.5 (Cγ), 70.9 ($CH_2C_6H_5$), 71.5 (Cα), 84.4 (Cβ), 109–151 (109.5, 112.1, 113.6, 118.2, 121.0, 121.5, 124.3, 127.2, 127.8, 127.9, 128.5, 129.7, 131.4, 132.5, 137.0, 144.7, 146.4, 147.5, 149.6, 151.4) (aromatic C), threo isomer: 21.7 ($H_3CC_6H_4$), 55.7 (OCH_3), 56.0 (OCH_3), 68.1 (Cγ), 70.9 ($CH_2C_6H_5$), 73.4 (Cα), 85.6 (Cβ), 110.2–150.8 (110.2, 112.1, 113.7, 119.4, 120.9, 121.4,

127.2, 127.9, 128.0, 128.6, 129.8, 131.8, 132.4, 137.0, 145.0, 147.3, 148.1, 150.0, 150.8) (aromatic C).

Tosylation of 4-*O*-Benzyl-syringylglycerol-β-syringyl Ether (Erythro Type) (**1b**)

4-*O*-Benzyl-syringylglycerol-β-syringyl ether (erythro type) (**1b**) (51.7 mg, 0.110 mM) were dissolved in 3 mL of dry pyridine, and then tosyl chloride (104.6 mg, 0.550 mM) was added. The reaction solution was kept at room temperature for 6.5 h, and worked-up by the standard method to afford colorless syrup, which was purified by PTLC developed with ethyl acetate–*n*-hexane (1:2, v/v) to give compound **2b** as a colorless syrup (67.2 mg, 98% yield). ^{1}H NMR δ ($CDCl_3$): 2.40 (3H, s, CH_3C$_6$H$_4$), 3.78 (6H, s, OCH_3), 3.86 (6H, s, OCH_3), 3.99 (H, dd, *J* 11.1, 3.3, Hγ), 4.30 (H, d, *J* 3.3, αOH), 4.37 (H, dd, *J* 11.1, 7.2, Hγ), 4.51 (H, m, Hβ), 4.82 (H, t, *J* 3.3, Hα), 5.00 (2H, s, CH_2C$_6$H$_5$), 6.51–7.50 (10H, m, aromatic H), 7.24 (2H, d, *J* 8.1, aromatic H of tosyl group), 7.61 (2H, d, *J* 8.1, aromatic H of tosyl group); ^{13}C NMR δ ($CDCl_3$): 21.6 (H$_3$*C*C$_6$H$_4$), 56.1 (OCH_3), 56.2 (OCH_3), 68.6 (Cγ), 71.7 (Cα), 75.0 (*C*H$_2$C$_6$H$_5$), 83.4 (Cβ), 103–154 (102.9, 105.5, 124.6, 127.80, 127.82, 128.1, 128.5, 129.6, 132.9, 133.9, 134.6, 136.0, 137.8, 144.6, 153.5, 153.6) (aromatic C).

Iodination of γ-*p*-Toluenesulfinyl-4-*O*-benzyl-guaiacylglycerol-β-guaiacyl Ether (**2a**)

Isomeric mixture of tosylate (**2a**) (58.0 mg, 0.103 mM) were dissolved in 3 mL of dry DMF, and then potassium iodide (341.4 mg, 0.515 mM) was added. The reaction solution was kept at 100°C for 1 h, and worked-up by the standard method to afford colorless syrup, which was purified by PTLC developed with ethyl acetate–*n*-hexane (1:2, v/v) to give compound **3a** as a colorless syrup (52.2 mg, 98% yield), which gave two spots of erythro and threo isomers (1:1). ^{1}H NMR δ ($CDCl_3$) of erythro isomer: 3.07 (H, dd, *J* 10.5, 4.2, Hγ), 3.47 (H, dd, *J* 10.5, 8.4, Hγ), 3.87 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 4.26 (H, ddd, *J* 8.4, 4.2, 3.3, Hβ), 4.87 (H, d, *J* 3.3, Hα), 5.14 (2H, s, CH_2C$_6$H$_5$), 6.76–7.44 (12H, m, aromatic H), threo isomer: 2.98 (H, dd, *J* 11.1, 3.0, Hγ), 3.40 (H, dd, *J* 11.1, 4.5, Hγ), 3.73 (H, ddd, *J* 7.5, 4.5, 3.0, Hβ), 3.906 (3H, s, OCH_3), 3.912 (3H, s, OCH_3), 3.98 (H, s, αOH), 4.93 (H, d, *J* 7.5, Hα), 5.16 (2H, s, CH_2C$_6$H$_5$), 6.84–7.45

(12H, m, aromatic H); ^{13}C NMR δ ($CDCl_3$) of erythro isomer: 3.81 (Cγ), 55.83 (OCH_3), 55.98 (OCH_3), 70.9 ($CH_2C_6H_5$), 72.3 (Cα), 87.4 (Cβ), 110–152 (109.7, 112.1, 113.7, 118.4, 121.2, 121.6, 124.5, 127.3, 127.8, 128.5, 131.7, 137.0, 146.4, 147.5, 149.6, 151.7) (aromatic C), threo isomer: 6.76 (Cγ), 55.80 (OCH_3), 56.03 (OCH_3), 70.9 ($CH_2C_6H_5$), 76.4 (Cα), 84.8 (Cβ), 110–151 (110.4, 112.3, 113.8, 119.4, 120.9, 121.3, 124.5, 127.3, 127.9, 128.5, 132.3, 137.0, 146.8, 148.1, 149.7, 151.1) (aromatic C).

Iodination of γ-*p*-Toluenesulfinyl-4-*O*-benzyl-syringylglycerol-β-syringyl Ether (**2b**)

Tosylate (erythro type) (**2b**) (32.2 mg, 0.0516 mM) was dissolved in 2 mL of dry DMF, and then potassium iodide (171.3 mg, 0.258 mM) was added. The reaction solution was kept at 100°C for 5 h, and worked-up by the standard method to afford colorless syrup, which was purified by PTLC developed with ethyl acetate–*n*-hexane (1/2, v/v) to give compound **3b** as a colorless syrup (28.9 mg, 97% yield). ^{1}H NMR δ ($CDCl_3$): 3.01 (H, dd, *J* 10.8, 4.8, Hγ), 3.56 (H, dd, *J* 10.8, 8.1, Hγ), 3.82 (6H, s, OCH_3), 3.90 (6H, s, OCH_3), 4.41 (H, m, Hβ), 4.50 (H, d, *J* 3.3, αOH), 4.86 (H, t, *J* 3.3, Hα), 5.00 (2H, s, $CH_2C_6H_5$), 6.57–7.48 (10H, m, aromatic H); ^{13}C NMR δ ($CDCl_3$): 2.29 (Cγ), 56.18 (OCH_3), 56.2 (OCH_3), 72.5 (Cα), 74.9 ($CH_2C_6H_5$), 85.3 (Cβ), 103–154 (103.3, 105.5, 124.6, 127.8, 128.1, 128.5, 134.6, 134.7, 136.1, 137.8, 153.5, 153.6) (aromatic C).

Zinc Treatment of γ-Deoxy-γ-iodo-4-*O*-benzyl-guaiacylglycerol-β-guaiacyl Ether (**3a**)

Isomeric mixtures of iodinate (**3a**) (34.0 mg, 0.0654 mM) were dissolved in 3 mL of dioxane–H_2O (9:1, v/v), and activated metal zinc dust (340 mg, 5.20 mM) was added. The reaction mixture was kept at 50°C for 2 h with vigorous stirring, and then filtered off to remove activated zinc dust. The filtrate was worked-up by the standard method to afford slightly yellow syrup, which contains olefinic compound **4a** and guaiacol. The products were purified by PTLC developed two times with ethyl acetate–*n*-hexane (1:4, v/v) to give compound **4a** as a colorless syrup (16.3 mg, 93% yield). Compound **4a**: ^{1}H NMR δ ($CDCl_3$): 3.87 (3H, s, OCH_3), 5.14 (H, d, *J* 5.4, Hα), 5.15 (2H, s, $CH_2C_6H_5$), 5.19 (H, m, H*cis*), 5.35 (H, dt, *J* 16.8, 1.5, 1.5, H*trans*), 6.04 (H, ddd, *J* 16.8, 10.5, 5.4, Hβ),

6.80–7.44 (8H, m, aromatic H); ^{13}C NMR δ ($CDCl_3$): 56.0 (OCH_3), 71.0 ($CH_2C_6H_5$), 75.1 (Cα), 115.0 (Cγ), 140.2 (Cβ), 110–149.8 (110.0, 113.8, 118.6, 127.2, 127.8, 128.5, 135.8, 137.1, 147.7, 149.8) (aromatic C).

Zinc Treatment of γ-Deoxy-γ-iodo-4-*O*-benzyl-syringylglycerol-β-syringyl Ether (**3b**)

Iodinate (erythro type) (**3b**) (15 mg, 0.0259 mM) was dissolved in 2 mL of dioxane–H_2O (9:1, v/v), and activated metal zinc dust (150 mg, 2.29 mM) was added. The reaction mixture was kept at 50°C for 2 h with vigorous stirring, and then filtered off to remove activated zinc dust. The filtrate was worked-up by the standard method to afford slightly yellow syrup, which contains olefinic compound **4b** and syringol. The products were purified by PTLC developed two times with ethyl acetate–*n*-hexane (1:4, v/v) to give compound **4b** as a colorless syrup (7.4 mg, 96% yield). Compound **4b**: ^{1}H NMR δ ($CDCl_3$): 3.84 (6H, s, OCH_3), 4.99 (2H, s, $CH_2C_6H_5$), 5.15 (H, d, *J* 6.0, Hα), 5.23 (H, dt, *J* 10.5, 1.5, 1.5, H*cis*), 5.38 (H, dt, *J* 17.1, 1.5, 1.5, H*trans*), 6.05 (H, ddd, *J* 17.1, 10.5, 6.0, Hβ), 6.60 (2H, s, aromatic H), 7.26–7.37 (3H, m, aromatic H), 7.48–7.51 (2H, m, aromatic H); ^{13}C NMR δ($CDCl_3$): 56.1 (OCH_3), 75.0 ($CH_2C_6H_5$), 75.5 (Cα), 115.4 (Cγ), 140.0 (Cβ), 103.2–153.6 (103.2, 127.8, 128.1, 128.5, 136.3, 137.8, 138.3, 153.6) (aromatic C).

Hydrogenation and Acetylation of 3-(4-*O*-Benzyl-guaiacyl)-3-hydroxy-1-propene (**4a**)

Olefinic compound **4a** (27.0 mg, 0.100 mM) was dissolved in 3 mL of dioxane–H_2O (9:1, v/v), and 10%Pd–C (27 mg) was added. The reaction mixture was kept at room temperature for 1 h with stirring under hydrogen, and filtered off. The filtrate was concentrated to dryness in vacuo. Compound **5a** was purified by PTLC developed with ethyl acetate–*n*-hexane (1:2, v/v) to give a colorless syrup (17.8 mg, 98% yield). Compound **5a** (17.8 mg, 0.0978 mM) was acetylated at room temperature for 1 h in 2 mL of acetic anhydride–pyridine (1:1, v/v). The solvent was removed completely by coevaporation with ethanol under reduced pressure to obtain compound **6a** (24.8 mg, 95% yield). Compound **6a**: ^{1}H NMR δ ($CDCl_3$): 0.90 (3H, t, *J* 7.2, Hγ), 1.84 (2H, m, Hβ), 2.09 (3H, s, γ-OAc), 2.32 (3H, s, Ph-OAc), 3.84 (3H, s, OCH_3), 5.65 (H, t, *J* 6.9, Hα), 6.95 (3H, m, aromatic H); ^{13}C NMR δ ($CDCl_3$): 10.1 (Cγ),

20.7 (Ph-OCO*C*H_3), 21.3 (α-OCO*C*H_3), 29.3 (Cβ), 55.9 (OCH_3), 77.2 (Cα), 110.8–150.9 (110.8, 118.9, 122.6, 139.2, 139.4, 150.9) (aromatic C), 169.1 and 170.4 (-O*C*OCH_3).

Hydrogenation and Acetylation of 3-(4-*O*-Benzyl-syringyl)-3-hydroxy-1-propene (**4b**)

Hydrogenation of compound **4b** (3.0 mg, 0.010 mM) with 10% Pd–C (10 mg) in 1 mL of dioxane–H_2O (9:1, v/v) was performed for 1 h followed by the same manner as hydrogenation of compound **4a** to afford compound **5b** (2.0 mg, 94% yield). Compound **5b** (2.0 mg, 0.00943 mM) was acetylated in a similar manner as compound **5a** to obtain compound **6b** (2.5 mg, 90% yield). Compound **6b**: ^{1}H NMR δ ($CDCl_3$): 0.91 (H, t, *J* 7.2, Hγ), 1.85 (H, m, Hβ), 2.09 (3H, s, α-OAc), 2.34 (3H, s, Ph-OAc), 3.83 (6H, s, OCH_3), 5.62 (H, dd, *J* 6.3, 6.1, Hα), 6.57 (2H, s, aromatic H); ^{13}C NMR δ ($CDCl_3$): 10.1 (Cγ), 20.5 (Ph-OCO*C*H_3), 21.3 (α-OCO*C*H_3), 29.4 (Cβ), 56.1 (OCH_3), 77.3 (Cα), 103.2–152.0 (103.2, 128.0, 139.0, 152.0) (aromatic C), 168.8 and 170.4 (-O*C*OCH_3).

Authentic Compounds

1-Guaiacyl-1-propanol Diacetate (**6a**)

4-*O*-Benzylvanillin (0.15 g, 0.62 mmol) was dissolved in anhydrous diethylether (10 mL), and ethylmagnesium bromide (0.25 mL (3 mol/L), 0.75 mmol) was added dropwise. The reaction mixture was kept at room temperature for 0.5 h with stirring. Then ammonium chloride (53.5 mg, 1 mmol)/water (1 mL) was added to decompose excess ethylmagnesium bromide. The reaction mixture was worked-up by the standard method to obtain a colorless substance. It was hydrogenated by the same manner of compound **5a**. The residue was acetylated in anhydrous acetic acid–pyridine (1:1, v/v) at room temperature overnight to obtain 1-guaiacyl-1-propanol diacetate (**6a**).

1-Syringyl-1-propane Diacetate Standard (**6b**)

4-*O*-Benzyl syringaldehyde (0.15 g, 0.55 mmol) was dissolved in anhydrous diethylether (10 mL), and ethylmagnesium bromide (0.22 mL (3 mol/L), 0.33 mmol) was added dropwise. The reaction mixture was

kept at room temperature for 0.5 h with stirring. The reaction mixture was worked-up in a similar manner as 1-guaiacyl-1-propanol diacetate (**5a**) to give 1-syringyl-1-propanol (**5b**), which was acetylated to afford 1-syringyl-1-propanol diacetate (**6b**).

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