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Phenolic constituents of *Taxus cuspidata* I: lignans from the roots

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Abstract The phenolic constituents of the roots of *Taxus cuspidata* (Japanese yew) were investigated. Four lignans, [(+)-taxiresinol (**1**), (+)-lariciresinol (**2**), (−)-secoisolariciresinol (**3**), and (+)-pinoresinol (**4**)] were isolated and identified. The assignment of proton and carbon atoms for the lignans were finally solved by one- and two-dimensional-nuclear magnetic resonance spectra. The enantiomeric excess of these lignans were determined by chiral high-performance liquid chromatographic analyses. (+)-Lariciresinol and (−)-secoisolariciresinol were optically pure; (+)-taxiresinol was also suggested to be optically pure, although (+)-pinoresinol was not (77% enantiomeric excess).

Key words *Taxus cuspidata* root · Lignan · (+)-Taxiresinol · (+)-Pinoresinol · Enantiomer

Introduction

The plants of the genus *Taxus* are evergreen gymnosperm, with eight species existing in the Northern Hemisphere. They are a rich source of biologically active diterpenoids belonging to the taxanes.[1–3] *Taxus cuspidata* Sieb. et Zucc. (Japanese yew, Taxaceae), widely distributed in Japan, has been used as a garden tree and for folk medicine.[4]

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The needles of *Taxus baccata* Linn. contain a phenylbutanoid glycoside rhododendrin, whose hepatoprotective activity might be due to its ability to act as an antioxidant.[5] The aqueous extracts from the needles of *T. baccata* also show tranquilizing and sedative activity, presumably related to the benzodiazepine-like activity of biflavones of the amentoflavone type.[6] To date, detailed investigations of the phenolic constituents of *T. cuspidata* had not been reported, in contrast to those of *T. baccata*. Mujumdar et al. isolated (+)-taxiresinol from the heartwood of *T. baccata* and determined its chemical structure.[7] However, the stereochemistry of (+)-taxiresinol has not been clarified.

In this study we isolated lignans from the roots of *T. cuspidata* and determined their structures and stereochemistry. The occurrence of the lignans were confirmed in the various parts of a *T. cuspidata* tree, and each content was quantified. The estimation of enantiomeric excess (e.e.) of the lignans in the roots is described.

Results and discussion

Four lignans (compounds **1**–**4**) (Fig. 1) were isolated from the roots of *T. cuspidata* by chromatographic methods without recrystallization. The structures of the compounds were elucidated mainly by analyzing ^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectra.

Compound **1** ($[\alpha]_D^{25}$ + 41.9°, ethanol), showed a molecular ion peak (M^+) at *m/z* 348 in its electron impact mass (EIMS) spectrum. The ^{1}H-NMR ($CDCl_3$-CD_3OD) spectrum was assigned with homonuclear (^{1}H-^{1}H) chemical shift-correlation spectroscopy (COSY). It was revealed that a doublet at δ 4.72 (J = 6.6 Hz, H-7′) and two double doublets at δ 3.66 and 3.83 (J = 10.8, 6.6 Hz, H-9′a; J = 10.8, 8.0 Hz, H-9′b) were coupled with the multiplet at δ 2.40 (H-8′). It was also revealed that four double doublets at δ 2.48, 2.94, 3.74, and 3.99 (J = 13.3, 11.7 Hz, H-7a; J = 13.3, 4.4 Hz, H-7b; J = 8.4, 6.0 Hz, H-9a; J = 8.4, 6.5 Hz, H-9b, respectively) were coupled with the multiplet at δ 2.74 (H-8). The

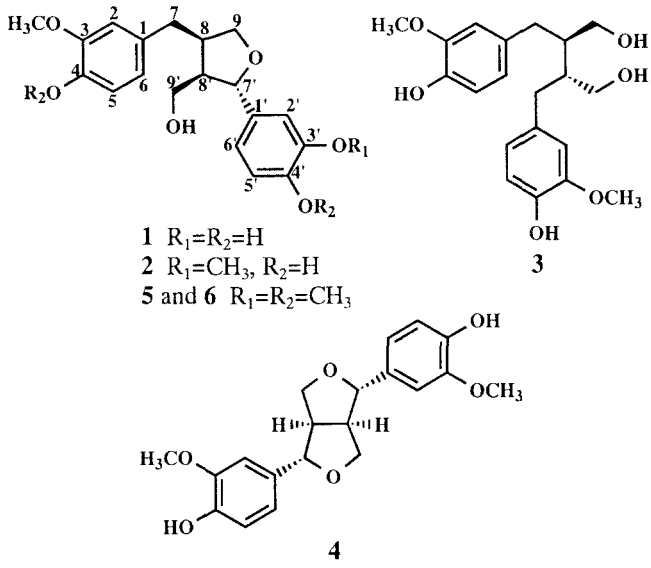

Fig. 1. Four lignans (**1**–**4**) isolated from the roots of *Taxus cuspidata* and derivatives (**5** and **6**) of lignans **1** and **2**

Table 1. Heteronuclear multiple bond connectivity (HMBC) correlations observed for compound **1** (^{1}H: 400 MHz, $CDCl_3$-CD_3OD)

H	Correlations to C
2	C-7, C-6, C-4, C-3
5	C-1
6	C-2, C-4
7a	C-8, C-2, C-6, C-1, C-9
7b	C-8, C-2, C-6, C-1, C-9
8	–
9a	C-8, C-7′
9b	C-8, C-7′
3-OCH_3	C-3
2′	C-6′, C-4′, C-3′
5′	C-1′
6′	C-7′, C-2′, C-4′
7′	C-8′, C-9′, C-8, C-2′, C-6′, C-1′
8′	C-8, C-9′, C-7′
9′a	C-8, C-8′, C-7′
9′b	C-8, C-8′, C-7′

^{1}H-NMR ($CDCl_3$) spectrum exhibited a singlet of an alcoholic hydroxyl group (δ 1.39) and three singlets of phenolic hydroxyl groups (δ 5.27, 5.43, 5.49). The assignment of the carbon atoms was established by heteronuclear (^{1}H-^{13}C) COSY and heteronuclear multiple bond connectivity (HMBC) spectroscopy (Table 1). The ^{13}C resonances of quaternary carbons C-1, C-1′, C-3, C-3′, C-4, and C-4′ were assigned completely. In this way, the structure for compound **1**, (+)-taxiresinol, was determined.

The ^{1}H and ^{13}C-NMR spectra of compound **2** ($[\alpha]_D^{25}$ + 19.8°, methanol) were similar to those of compound **1** except for the existence of two methoxyl groups. The mass spectrum of compound **2** showed a molecular ion peak at *m/z* 360 that was greater than that of taxiresinol (*m/z* 346) because of an additional CH_2 moiety. The structure of compound **2** therefore was determined to be (+)-lariciresinol.

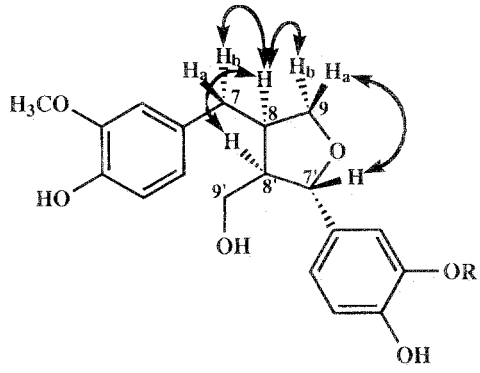

Fig. 2. Key nuclear Overhauser enhancements (NOEs) of taxiresinol (**1**, R = H) and lariciresinol (**2**, R = CH_3)

Table 2. Contents of lignans in various parts of *Taxus cuspidata*

Plant part	Extracts (%)[a]	Lignans (%)[a]			
		1	**2**	**3**	**4**
Roots	13.17	0.176	0.033	0.041	0.001
Wood	6.41	0.655	0.174	0.193	0.002
Bark	29.70	–	–	–	–
Twigs	17.55	0.151	0.056	0.116	0.002
Needles	52.56	0.037	–	0.095	–

[a]Percentages are based on oven-dried matter

Compounds **3** and **4** were identified as (−)-secoisolariciresinol and (+)-pinoresinol, respectively, by comparison of their $[\alpha]_D^{25}$, ultraviolet (UV), infrared (IR), EIMS, and NMR spectral properties with those in the literature.[8,9] The isolation of known lignans **1**, **2**, and **4** from *T. cuspidata* was the first case, although the existence of **2** in this plant had been confirmed by chromatographic methods, previously.[10,11]

The nuclear Overhauser enhancement (NOE) difference spectroscopic experiments for taxiresinol (**1**) and lariciresinol (**2**) were performed to show the spatial relations of protons. The key NOEs of these lignans are shown in Fig. 2. The conformations of taxiresinol were determined as 8,8′-*cis* and 7′,8′-*trans* from the observed NOEs and were similar to lariciresinol. The abusolute configulations of (+)-lariciresinol (**2**), (−)-secoisolariciresinol (**3**), and (+)-pinoresinol (**4**) were known to be (7′*S*,8*R*,8′*R*), (8*R*,8′*R*), and (7*S*,7′*S*,8*R*,8′*R*,), respectively.[12] Taxiresinol (**1**) and lariciresinol (**2**), isolated as before, were *O*-methylated by trimethylsilyldiazomethane to determine the absolute configuration of taxiresinol. The ^{1}H-NMR spectrum and the optical rotation of taxiresinol trimethyl ether (**5**) were identical with those of lariciresinol dimethyl ether (**6**). Therefore, the absolute configuration of (+)-taxiresinol was confirmed to be (7′*S*,8*R*,8′*R*).

The content of the lignans in the various parts of a *T. cuspidata* tree were quantitatively analyzed by reversed phase high-performance liquid chromatography (HPLC) (Table 2). The contents of lignans **1**–**4** were higher in the wood and the roots than in the other plant parts of a *T. cuspidata* tree, and they were not detected in the bark. The content of taxiresinol in the wood was significantly high.

The enantiomeric excess of the lignans in the roots of *T. cuspidata* were determined by chiral HPLC analyses. Lariciresinol and (−)-secoisolariciresinol were optically pure; (+)-taxiresinol was also suggested to be optically pure, however, (+)-pinoresinol was not optically pure (77% e.e.). Furthermore, the optical rotations of taxiresinol trimethyl ether (**5**) were agreed with those of lariciresinol dimethyl ether (**6**). The highly enantiospecific reduction step, conversion of (+)-pinoresinol to (+)-lariciresinol in *Forsythia intermedia*, has been reported.[13] The taxiresinol obtained in this study was optically pure. Taxiresinol is the lignan with a catechol and guaiacyl nucleus. Recently, feeding experiments of [8-^{2}H] caffeic acid on axenic culture of a liverwort, *Lophocolea heterophylla*, had shown that (−)-1-(3,4-dihydroxyphenyl)-6,7-dihydroxy-1,2-dihydro-2,3-naphthalenecarboxylic acid was derived from the coupling of two molecules of caffeic acid.[14] Davin *et al.* reported that a combination of a dirigent protein (78 kDa) and an oxidase catalyzed the stereoselective coupling of bimolecular phenoxy radicals from coniferyl alcohol to afford optically pure (+)-pinoresinol in *Forsythia intermedia*, and that this coupling was substrate specific.[15] A lignan having a catechol nucleus (e.g., taxiresinol) could possibly be formed by the coupling of bimolecular phenylpropanoid monomers having catechol nuclei. If this assumption is correct, a new type of dirigent protein may exist, and the biosysthesis of lignans with a catechol nucleus is interesting.

Experimental

^{1}H- and ^{13}C-NMR spectra were obtained with a JEOL JNM-LA400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained with a JEOL JMS-DX303HF mass spectrometer. Ultraviolet spectra were measured with a Shimadzu UV-3100PC UV-VIS-NIR scanning spectrophotometer. Infrared spectra were recorded on a JASCO FT/IR-620 FT-IR spectrophotometer. Optical rotations were determined with a Horiba SEPA-300 or a JASCO DIP-140 (for lignans **5** and **6**) polarimeters. Analytical HPLC was performed with a system of Shimadzu LC-10AD pump, SPD-M10A UV detector, and OTO-10A column oven using a column prepacked Waters μ Bondasphere 5μ C_{18} 100Å (150 × 3.9 mm i.d.) and chiral columns prepacked Daicel Chiralcel OD (for lignans **1**, **3**, and **4**) or Chiralcel OC (for lignans **1** and **2**) (each 250 × 4.6 mm i.d.). Preparative HPLC was performed with a system of Shimadzu LC-6AD pump, SPD-10AV UV detector, and OTO-10A column oven using a column prepacked Waters μ Bondasphere 5μ C_{18} 100Å (150 × 19.0 mm i.d.). Column chromatography were employed with silica gel (Merck, Kieselgel 60, 70–230 mesh).

Plant material

16-Year-old *Taxus cuspidata* trees cultivated in Monbetsu, Hokkaido, Japan were sampled in June 1996 at random from throughout the cultivar block. They were divided into roots, wood, bark, twigs, and needles. The plant samples were crushed with a Willy mill-type crusher (Retsh, cutting mill SM1) and sieved to give meal of 40–60 meshes, which was air-dried (moisture content 12.3%).

Extraction and isolation

The sample powder of air-dried root (4.20 kg) was extracted three times with methanol (MeOH) dichloromethane (CH_2Cl_2) (1:1, v/v) at room temperature for 72 h. The combined MeOH/CH_2Cl_2 solution was filtered and evaporated in vacuo to give residual extract (485 g). The extract (85.00 g) was extracted successively with *n*-hexane and ethyl acetate (EtOAc) (each five times). After removing solvent from the combined extracts, *n*-hexane- (2.51 g) and EtOAc (38.09 g) soluble fractions and the EtOAc insoluble fraction (33.02 g) were obtained.

The EtOAc soluble fraction (10.00 g) was subjected to column chromatography with a gradient elution of benzene-EtOAc 9:1 → 0:10 (v/v), and 95 fractions were collected in 100-ml portions. Eluates (nos. 43–50) were subjected to reverse-phase preparative HPLC (PHPLC) (flow rate 12.0 ml/min; detection UV at 228 nm) (MeOH/H_2O, 45:55, v/v) to give colorless amorphous taxiresinol (**1**) (154.8 mg) and secoisolariciresinol (**3**) (67.2 mg). Eluates (nos. 25–26) were subjected to PHPLC (MeOH/H_2O, 43:57, v/v) to afford the colorless amorphous lariciresinol (**2**) (50.7 mg). Eluates (nos. 9–21) were subjected to PHPLC to elute fractions 1–11. Fraction 6 (6.4 mg) was subjected to PHPLC (MeOH/H_2O, 40:60, v/v) to afford the colorless amorphous pinoresinol (**4**) (2.5 mg).

Analytical HPLC method

Solvents for HPLC were HPLC grade (Wako Chemical Co.). The specifications of peaks for taxiresinol (**1**), lariciresinol (**2**), secoisolariciresinol (**3**), and pinoresinol (**4**) were set with co-HPLC analysis, using the lignans isolated from the roots of *T. cuspidata*. The quantitative determination by reverse-phase HPLC was based on calibration curves prepared previously with the lignans isolated from the roots of *T. cuspidata*. The eluent and conditions for analyses were as follows: eluent, MeOH/0.2% H_3PO_4 in H_2O (35:65, v/v); flow rate, 0.5 ml/min; detection, UV at 280 nm; column oven temperature, 40°C. The retention volumes (ml) of the lignans were as follows: taxiresinol (5.7), lariciresinol (10.0), secoisolariciresinol (11.3), and pinoresinol (17.5). The eluents and conditions for chiral HPLC analyses of the lignans were as follows [lignan, eluent (v/v), flow rate (ml/min)]: taxiresinol (**1**), *n*-hexane/1% AcOH in ethanol (EtOH) (70:30), 0.8; lariciresinol (**2**), *n*-hexane/EtOH (20:80), 0.4[16]; secoisolariciresinol (**3**), *n*-hexane-EtOH (70:30), 0.8[17]; pinoresinol (**4**), EtOH, 0.4[17]; detection, UV at 280 nm; column oven temperature, 25°C. The retention volumes (ml) of the lignans were as follows: (+)-taxiresinol (13.1), (+)-lariciresinol (8.0), (−)-secoisolariciresinol (7.4), (+)-pinoresinol (13.7), and (−)-

pinoresinol (5.7). For chiral HPLC analyses of (+)-taxiresinol, both Daicel Chiralcel OD and Chiralcel OC chiral columns were used; and the ratio of solvents (*n*-hexane/1% AcOH in ethanol or isopropanol) as eluents was varied from 10:90 to 100:0. All of the eluents showed a single peak, and it was considered that (+)-taxiresinol was optically pure.

(7′*S*,8*R*,8′*R*)-(+)-Taxiresinol (**1**)

Colorless powder, $[\alpha]_D^{25}$ = +41.9° (*c* = 2.00, EtOH)[lit.[7] +32.2°, EtOH]. UV λ_{max}^{MeOH} nm (logε): 282.2 (4.00), 225.2 (4.36), and 204.6 (4.69). IR ν_{max}^{KBr} cm^{-1}: 3361 (OH), 1606, 1515, 1451, 1433, 1370, 1278, 1237, 1154, 1115, 1034, and 814. ^{1}H-NMR ($CDCl_3$-CD_3OD): δ 2.40 (1H, *m*, H-8′), 2.48 (1H, *dd*, *J* = 13.3, 11.7 Hz, H-7a), 2.74 (1H, *m*, H-8), 2.94 (1H, *dd*, *J* = 13.3, 4.4 Hz, H-7b), 3.66 (1H, *dd*, *J* = 10.8, 6.6 Hz, H-9′a), 3.74 (1H, *dd*, *J* = 8.4, 6.0 Hz, H-9a), 3.83 (1H, *dd*, *J* = 10.8, 8.0 Hz, H-9′b), 3.86 (3H, *s*, 3-OCH_3), 3.99 (1H, *dd*, *J* = 8.4, 6.5 Hz, H-9b), 4.72 (1H, *d*, *J* = 6.6 Hz, H-7′), 6.65 (1H, *dd*, *J* = 8.3, 2.0 Hz, H-6), 6.68 (1H, *dd*, *J* = 8.1, 2.0 Hz, H-6′), 6.74 (1H, *d*, *J* = 2.0 Hz, H-2), 6.768 (1H, *d*, *J* = 8.1 Hz, H-5′), 6.772 (1H, *d*, *J* = 8.3 Hz, H-5), and 6.80 (1H, *d*, *J* = 2.0 Hz, H-2′). ^{1}H-NMR ($CDCl_3$): δ 1.39 (1H, *s*, 9′-OH, disappeared with addition of D_2O), 2.38 (1H, *m*, H-8′), 2.54 (1H, *dd*, *J* = 13.5, 10.5 Hz, H-7a), 2.72 (1H, *m*, H-8), 2.90 (1H, *dd*, *J* = 13.5, 5.1 Hz, H-7b), 3.74 (1H, *dd*, *J* = 8.5, 6.3 Hz, H-9a), 3.78 (1H, overlap, H-9′a), 3.88 (1H, *s*, 3-OCH_3), 3.90 (1H, overlap, H-9′b, turned into *dd* (*J* = 10.7, 6.6 Hz) with addition of D_2O), 4.04 (1H, *dd*, *J* = 8.5, 6.6 Hz, H-9b), 4.77 (1H, *d*, *J* = 6.34 Hz, H-7′), 5.27, 5.43 (2H, each *s*, 3′-OH, 4′-OH, disappeared with addition of D_2O), 5.49 (1H, *s*, 4-OH, disappeared with addition of D_2O), 6.68 (1H, overlap, H-2), 6.69 (1H, overlap, H-6), 6.75 (1H, *dd*, *J* = 8.1, 2.0 Hz, H-6′), 6.82 (1H, *d*, *J* = 8.1 Hz, H-5′), 6.84 (1H, *d*, *J* = 8.1 Hz, H-5), and 6.87 (1H, *d*, *J* = 2.0 Hz, H-2′). NOE ($CDCl_3$-CD_3OD): see Fig. 2. ^{13}C-NMR ($CDCl_3$-CD_3OD): δ 32.33 (C-7), 41.96 (C-8), 52.08 (C-8′), 55.26 (OCH_3), 59.17 (C-9′), 72.12 (C-9), 82.26 (C-7′), 111.60 (C-2), 112.54 (C-2′), 114.54 (C-5), 114.64 (C-5′), 117.21 (C-6′), 120.65 (C-6), 131.83 (C-1), 134.14 (C-1′), 143.76 (C-4′), 143.78 (C-4), 144.27 (C-3′), and 146.95 (C-3). HMBC ($CDCl_3$-CD_3OD): see Table 1. MS *m/z* [rel. int. (%)]: 346 (84, M^+), 328 (6), 180 (40), 164 (17), and 137 (100).

(7′*S*,8*R*,8′*R*)-(+)-Taxiresinol trimethyl ether (**5**)

O-Methylation of (+)-taxiresinol (**1**) with trimethylsilyldiazomethane and *N*,*N*-diisopropylethylamine[18] gave corresponding trimethyl ether (**5**). Colorless oil, $[\alpha]_D^{25}$ = +24.1° (*c* = 0.40, acetone). ^{1}H-NMR ($CDCl_3$): δ 1.39 (1H, *t*, *J* = 5.0 Hz, 9′-OH, disappeared with addition of D_2O), 2.43 (1H, *m*, H-8′), 2.58 (1H, *dd*, *J* = 13.4, 10.7 Hz, H-7a), 2.76 (1H, *m*, H-8), 2.94 (1H, *dd*, *J* = 13.4, 5.1 Hz, H-7b), 3.76 (1H, *dd*, *J* = 8.5, 6.1 Hz, H-9a), 3.80 (1H, *m*, H-9′a, turned into *dd* (*J* = 10.7, 6.6 Hz) with addition of D_2O), 3.86 (1H, *s*, 4-OCH_3), 3.870 (1H, *s*, 3-OCH_3), 3.873 (1H, *s*, 4′-OCH_3), 3.89 (1H, *s*, 3′-OCH_3), 3.93 (1H, *ddd*, *J* = 10.7, 6.8, 4.9 Hz, H-9′b, turned into *dd* (*J* = 10.7, 7.1 Hz) with addition of D_2O), 4.07 (1H, *dd*, *J* = 8.5, 6.6 Hz, H-9b), 4.82 (1H, *d*, *J* = 6.6 Hz, H-7′), 6.72 (1H, *d*, *J* = 1.8 Hz, H-2), 6.74 (1H, *dd*, *J* = 8.1, 1.8 Hz, H-6), 6.80 (1H, *d*, *J* = 8.1 Hz, H-5), 6.83 (1H, *d*, *J* = 8.1 Hz, H-5′), 6.87 (1H, overlap, H-6′), and 6.89 (1H, overlap, H-2′). ^{13}C-NMR ($CDCl_3$): δ 33.27 (C-7), 42.35 (C-8), 52.57 (C-8′), 55.89 (4-OCH_3), 55.91 (3-OCH_3), 55.94 (4′-OCH_3), 60.85 (3′-OCH_3), 60.99 (C-9′), 72.95 (C-9), 82.76 (C-7′), 108.96 (C-2′), 111.01 (C-5′), 111.32 (C-5), 111.92 (C-2), 118.03 (C-6′), 120.48 (C-6), 132.95 (C-1), 135.42 (C-1′), 147.48 (C-4), 148.44, 148.98 (C-4′,3), and 149.11 (C-3′).

(7′*S*,8*R*,8′*R*)-(+)-Lariciresinol (**2**)

Colorless powder, $[\alpha]_D^{25}$ = +19.8° (*c* = 1.00, MeOH), >99% e.e. UV λ_{max}^{MeOH} nm (logε): 282.2 (4.00), 225.2 (4.36), and 204.6 (4.69). IR ν_{max}^{KBr} cm^{-1}: 3365 (OH), 1603, 1516, 1458, 1432, 1371, 1272, 1237, 1155, 1124, 1034, and 817. ^{1}H-NMR ($CDCl_3$): δ 1.38 (1H, *t*, *J* = 5.1 Hz, 9′-OH, disappeared with addition of D_2O), 2.41 (1H, *m*, H-8′), 2.55 (1H, *dd*, *J* = 13.7, 10.7 Hz, H-7a), 2.74 (1H, *m*, H-8), 2.92 (1H, *dd*, *J* = 13.7, 5.1 Hz, H-7b), 3.75 (1H, *dd*, *J* = 8.5, 6.1 Hz, H-9a), 3.78 (1H, overlap, H-9′a, turned into *dd* (*J* = 10.7, 6.6 Hz) with addition of D_2O), 3.87 (3H, *s*, 3-OCH_3), 3.89 (3H, *s*, 3′-OCH_3), 3.92 (1H, *ddd*, *J* = 11.0, 7.1, 4.9 Hz, H-9′b, turned into *dd* (*J* = 10.7, 7.1 Hz) with addition of D_2O), 4.06 (1H, *dd*, *J* = 8.5, 6.6 Hz, H-9b), 4.79 (1H, *d*, *J* = 6.6 Hz, H-7′), 5.50 (1H, *s*, 4-OH, disappeared with addition of D_2O), 5.57 (1H, *s*, 4′-OH, disappeared with addition of D_2O), 6.69 (1H, *d*, *J* = 1.9 Hz, H-2), 6.70 (1H, *dd*, *J* = 8.5, 1.9 Hz, H-6), 6.81 (1H, *J* = 8.1, 1.8 Hz, H-6′), 6.84 (1H, *d*, *J* = 8.5 Hz, H-5), 6.87 (1H, *d*, *J* = 1.8 Hz, H-2′), and 6.88 (1H, *d*, *J* = 8.1 Hz, H-5′). NOE ($CDCl_3$-CD_3OD): see Fig. 2. ^{13}C-NMR ($CDCl_3$-CD_3OD): δ 32.48 (C-7), 42.07 (C-8), 52.15 (C-8′), 55.37 (2 × OCH_3), 59.30 (C-9′), 72.30 (C-9), 82.46 (C-7′), 108.76 (C-2′), 111.63 (C-2), 114.43 (C-5′), 114.61 (C-5), 118.28 (C-6′), 120.74 (C-6), 131.85 (C-1), 134.02 (C-1′), 143.90 (C-4), 145.10 (C-4′), 146.99 (C-3), and 147.08 (C-3′). MS *m/z* [rel. int. (%)]: 360 (97, M^+), 194 (31), 175 (18), 153 (32), and 137 (100).

(7′*S*,8*R*,8′*R*)-(+)-Lariciresinol dimethyl ether (**6**)

O-Methylation of (+)-lariciresinol (**1**) with trimethylsilyldiazomethane and *N*,*N*-diisopropylethylamine[18] gave corresponding dimethyl ether (**6**). Colorless oil, $[\alpha]_D^{25}$ = +22.5° (*c* = 0.35, acetone). The NMR spectral properties were completely identical to those of *(+)-taxiresinol trimethyl ether* (**5**).

(8*R*,8′*R*)-(−)-Secoisolariciresinol (**3**)

Colorless powder, $[\alpha]_D^{25}$ = −36.4° (*c* = 1.00, acetone), >99% e.e. MS *m/z* [rel. int. (%)]: 362 (74, M^+), 344 (22), and 137 (100). The NMR spectral properties were identical to those in the literature.[8]

(7*S*,7′*S*,8*R*,8′*R*,)-(+)-Pinoresinol (**4**)

Colorless powder, $[\alpha]_D^{25} = +55.2°$ (c = 0.35, $CHCl_3$), 77% e.e., MS *m/z* [rel. int. (%)]: 358 (100, M^+), 205 (21), 163 (36), 151 (78), and 137 (45). The NMR spectral properties were identical to those in the literature.[9]

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