New Phenylpropanoid Glycosides from *Juniperus communis* var. *depressa*

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Two new phenylpropanoid glycosides were isolated from the leaves and stems of *Juniperus communis* var. *depressa* (Cupressaceae) along with 14 known compounds. Their structures were determined by spectral analyses, in particular by 2D-NMR spectral evidence.

Key words *Juniperus communis* var. *depressa*; Cupressaceae; phenylpropanoid glycoside; lignan glycoside

In a survey of chemical components from useful plants grown in western North America, we have reported a number of chemical compounds (nine phenylpropanoids, six neolignans, fourteen flavonoids, seven catechins, and five terpenoids) from the leaves and stems of *Juniperus communis* var. *depressa* (Cupressaceae).[2—6)] In our continuing study on this plant, two new phenylpropanoid glycosides (**1** and **4**), were isolated together with six known phenyl propanoides (**2**, **3**, **5**—**8**), two known phenolic compounds (**9**, **10**), and six known lignans (**11**—**16**). This paper describes the structural elucidation of the new compounds as well as the characterization of the absolute structures of three lignans (**11**, **12**, **14**) based on NMR and circular dichroism (CD) spectral evidence.

The *n*-BuOH soluble part of the MeOH extract was separated by a combination of silica gel, octadecyl silica gel (ODS), and Sephadex LH-20 column chromatographies, followed by HPLC separation, to afford two new compounds (**1** and **4**) and 14 known compounds (**2**, **3**, **5**—**16**). The known compounds were identified as junipediol B 8-*O*-β-D-glucopyranoside (**2**),[7)] junipediol A 8-*O*-β-D-glucopyranoside (**3**),[7)] (7*S*,8*S*)-guaiacylglycerol (**5**),[8,9)] junipetrioloside A (**6**),[10)] *trans*-coniferyl aldehyde (**7**),[11)] 2-[4-(3-hydroxypropyl)-2-methoxyphenoxy]-1,3-propanediol (**8**),[12)] vanillin (**9**),[13)] arbutin (**10**),[13)] (2*S*,3*R*)-2,3-dihydro-7-hydroxy-3-hydroxymethyl-2-(4′-hydroxy-3′-methoxyphenyl)-5-benzofuranpropanol 4′-*O*-β-D-glucopyranoside (**13**),[14)] (2*R*,3*S*)-2,3-dihydro-3-hydroxymethyl-7-methoxy-2-(4′-hydroxy-3′-methoxyphenyl)-5-benzofuranpropanol 4′-*O*-β-D-glucopyranoside (**15**),[15)] and cupressoside A (**16**)[16)] by comparison of physical data with literature values and spectroscopic evidence. The structures of the isolates (**1**—**16**) are given in Chart 1.

Compound **1**, a white amorphous powder, showed the $[M-H]^-$ ion peak at *m*/*z* 489.1604 in the negative ion high resolution (HR) FAB-MS, indicating the molecular formula to be $C_{21}H_{30}O_{13}$. The ^{1}H- and ^{13}C-NMR spectral data (Table 1) showed the presence of a β-D-glucopyranosyl and an α-L-arabinofuranosyl moieties in **1**. Identification of monosaccharides, including its absolute configuration, was carried out by direct HPLC analysis of the acid hydrolysate. The ^{1}H-NMR and ^{1}H–^{1}H correlation spectroscopy (COSY) spectra of **1** showed the presence of a 1,2,4-trisubstituted benzene ring [δ 6.83 (1H, s, H-2), 6.73 (1H, d, J=8.1 Hz, H-5), and 6.75 (1H, br d, J=8.1 Hz, H-6)], aliphatic CH_2OH–CH(Ar)–CH_2O-moiety [δ 3.02 (1H, m, H-7), 4.07 (1H, dd, J=10.6, 7.6 Hz, H-8a), 3.77 (1H, dd, J=10.6, 4.0 Hz, H-8b), 3.84 (1H, dd, J=11.6, 5.5 Hz, H-9a), and 3.73 (1H, overlapping signal, H-9b)], and a methylenedioxy group [δ 5.88 (2H, s, H_2-10)] (Table 1). In addition, long-range correlations between H-7/C-1 and H_2-10/C-3, C-4 were observed in the heteronuclear multiple bond correlation spectroscopy (HMBC) spectrum (Fig. 1). Based on this spectral evidence, the aglycone of **1** was determined to be junipediol B.[7)] The position of the glycosyl moiety in **1** was decided by the following HMBC and nuclear Overhauser enhancement spectroscopy (NOESY) experiments (Fig. 1), in which the HMBC correlations (H-1′/C-8 and H-1″/C-6′) as well as the NOESY correlations (H-1′/H_2-8 and H-1″/H_2-6′) were observed. Therefore the α-L-arabinofuranosyl-(1→6)-β-D-glucopyranosyl moiety was connected to 8-hydroxyl group of junipediol B through a glycosidic bond. In the ^{1}H- and ^{13}C-NMR spectrum, anomeric proton and anomeric carbon signals of both glucose and arabinose in **1** appeared as sets of signals, respectively. This is attributed to the presence of the diastereomers as a result of the glycosidation at 8-hydroxy group of the achiral junipediol B.[7)] Attempts to separate both diastereomers were unsuccessful. In conclusion, the structure of **1** was determined to be junipediol B 8-*O*-(6′-*O*-α-L-arabinofuranosyl)-β-D-glucopyranoside.

Compound **4**, a white amorphous powder, showed the $[M-H]^-$ ion peak at *m*/*z* 427.1615 in the negative ion HR-FAB-MS, corresponding to the molecular formula of $C_{20}H_{28}O_{10}$. The ^{1}H- and ^{13}C-NMR spectra of **4** closely resembled those of rosarin [=*trans*-cinnamyl alcohol 9-*O*-(6′-*O*-α-L-arabinofuranosyl)-β-D-glucopyranoside] isolated from the same plant.[3)] However, in the ^{1}H-NMR spectrum, the coupling constant between H-7 and H-8 (J=11.6 Hz) in **4** was smaller than that of rosarin (J=15.9 Hz), indicating the H-7/H-8 *cis* configuration of the aglycone. Thus the structure of **4** was concluded to be *cis*-cinnamyl alcohol 9-*O*-(6′-*O*-α-L-arabinofuranosyl)-β-D-glucopyranoside.

Compound **11**, a white amorphous powder, gave the $[M-H]^-$ ion peak at *m*/*z* 545.1667 in the negative ion HR-FAB-MS, indicating the molecular formula to be $C_{27}H_{30}O_{12}$. In addition, the negative ion FAB-MS gave a fragment peak

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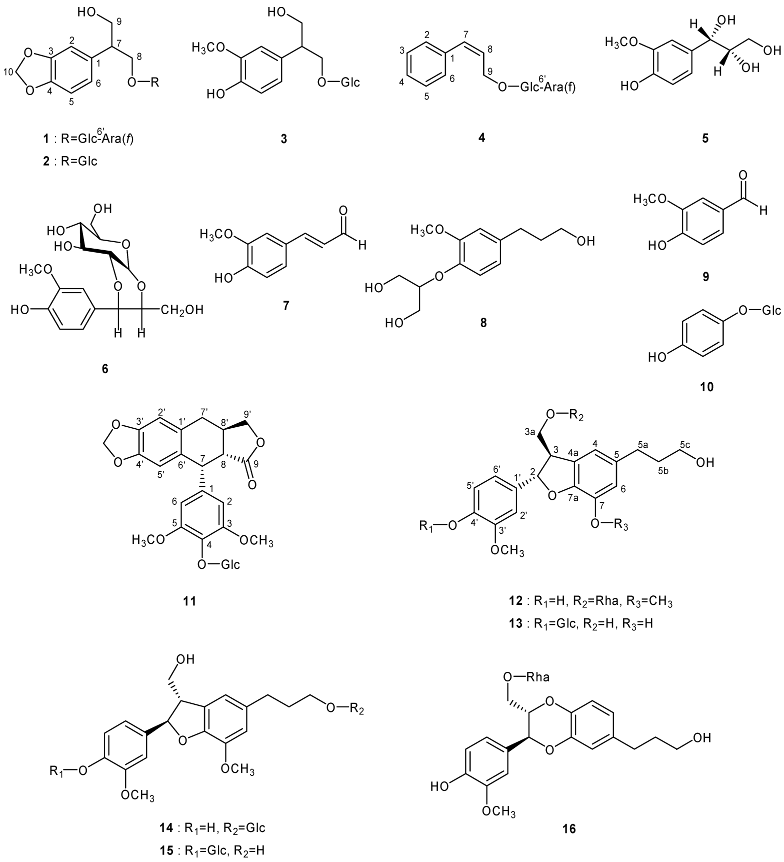

Chart 1

Table 1. ^{1}H- (600 MHz) and ^{13}C-NMR (150 MHz) Spectral Data of **1** and **4** in MeOH-d_4

No.	**1** δ_H	**1** δ_C	**4** δ_H	**4** δ_C
1		135.9		137.9
2	6.83 (s)	109.7	7.23—7.26 (m)$^{a)}$	129.9
3		149.0	7.35 (br dd, 7.6, 7.6)	129.4
4		147.7	7.23—7.26 (m)$^{a)}$	128.3
5	6.73 (d, 8.1)	109.0	7.35 (br dd, 7.6, 7.6)	129.4
6	6.75 (br d, 8.1)	122.6	7.23—7.26 (m)$^{a)}$	129.9
7	3.02 (m)	49.2	6.61 (br d, 11.6)	132.8
8	4.07 (dd, 10.6, 7.6)	72.2	5.90 (ddd, 11.6, 6.9, 6.0)	129.4
	3.77 (dd, 10.6, 4.0)			
9	3.84 (dd, 11.6, 5.5)	64.8	4.63 (ddd, 12.8, 6.0, 1.8)	67.4
	3.73$^{a)}$		4.44 (ddd, 12.8, 6.9, 1.8)	
10	5.88 (s)	102.1		
Glc 1′	4.28 (d, 7.8),	104.6,	4.32 (d, 7.8)	103.9
	4.29 (d, 7.8)$^{b)}$	104.9$^{b)}$		
2′	3.17 (dd, 9.0, 7.8)	75.1	3.19 (dd, 9.0, 7.8)	75.1
3′	3.32 (dd, 9.0, 9.0)	78.0	3.34 (dd, 9.0, 9.0)	78.0
4′	3.26 (dd, 9.0, 9.0)	72.0	3.29 (dd, 9.0, 9.0)	71.9
5′	3.44 (ddd, 9.0, 5.5, 2.5)	76.8	3.40 (ddd, 9.0, 5.7, 2.3)	76.7
6′	4.02 (dd, 11.6, 2.5)	68.2	3.98 (dd, 11.2, 2.3)	68.0
	3.58 (dd, 11.6, 5.5)		3.60 (dd, 11.2, 5.7)	
Ara (*f*) 1″	4.96 (br s),	110.0,	4.94 (d, 1.5)	109.9
	4.95 (br s)$^{b)}$	109.8$^{b)}$		
2″	3.99 (dd, 3.6, 1.0)	83.2	3.98 (dd, 3.3, 1.5)	83.1
3″	3.82 (dd, 5.6, 3.6)	78.9	3.81 (dd, 5.5, 3.3)	78.9
4″	3.96 (ddd, 5.6, 5.6, 4.0)	85.9	3.95 (ddd, 5.5, 5.5, 3.3)	85.9
5″	3.77 (dd, 11.6, 4.0)	63.1	3.72 (dd, 11.8, 3.3)	63.1
	3.61 (dd, 11.6, 5.6)		3.62 (dd, 11.8, 5.5)	

a) Overlapping with other signals. *b*) Appeared as sets of signals.

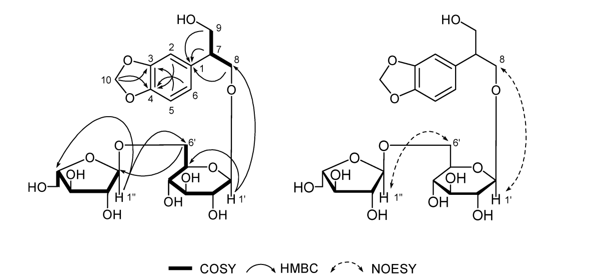

Fig. 1. Selected 2D NMR Sspectral Data of **1**

at *m/z* 383 due to the loss of a hexosyl unit from the $[M-H]^-$ ion. The ^{1}H- and ^{13}C-NMR spectral data exhibited the presence of a β-D-glucopyranosyl moiety as the sugar part (Table 2). The ^{1}H-NMR and ^{1}H–^{1}H COSY spectra indicated the presence of a 1,2,3,5-tetrasubstituted benzene ring [δ 6.33 (2H, br s, H-2 and H-6)], a 1,2,4,5-tetrasubstituted benzene ring [δ 6.62 (1H, s, H-2′) and 6.34 (1H, s, H-5′)], two methoxy groups [δ 3.63 (6H, s)], a methylenedioxy group [δ 5.80 (1H, d, J=1.2 Hz) and 5.79 (1H, d, J=1.2 Hz)], and aliphatic [–CH_2–CH(CH_2)–CH(CO)–(C)CH(C)–] proton signals as the aglycone moiety of **11** (Table 2). The ^{1}H–^{1}H COSY and HMBC correlations (Fig. 2) indicated that the plane structure of the aglycone of **11** was the same as that of 4-demethyldeoxypodophyllotoxin. The HMBC and NOESY correlations (Fig. 2) indicated that the β-D-glucosyl moiety was linked to the 4-OH of the aglycone through a glycosidic bond. The absolute configurations of the three chiral centers of the aglycone were determined as follows. Klyne *et al.* reported that 7α-aryl (=7*R*) derivatives in 7-aryltetralin type

Table 2. ^{1}H- (600 MHz) and ^{13}C-NMR (150 MHz) Spectral Data of **11** in MeOH-d_4

No.	11	
	δ_H	δ_C
1		139.3
2	6.33 (s)	110.2
3		153.5
4		135.3
5		153.5
6	6.33 (s)	110.2
7	4.48 (d, 5.4)	45.0
8	2.81 (dd, 13.8, 5.4)	48.3
9		177.7
1′		130.4
2′	6.62 (s)	109.6
3′		148.5
4′		148.1
5′	6.34 (s)	111.1
6′		131.9
7′	2.70 (dd, 16.2, 11.4)	33.6
	2.98 (dd, 16.2, 5.4)	
8′	2.61 (m)	34.4
9′	3.88 (dd, 10.8, 8.4)	73.6
	4.35 (dd, 8.4, 7.2)	
3,5-OCH_3	3.63 (6H, s)	57.0
O-CH_2-O	5.79 (d, 1.2)	102.5
	5.80 (d, 1.2)	
Glc 1″	4.74 (d, 7.8)	105.5
2″	3.35 (dd, 9.0, 9.0)	75.7
3″	3.31 (dd, 9.0, 9.0)	77.8
4″	3.32 (dd, 9.3, 9.0)	71.3
5″	3.10 (ddd, 9.0, 4.8, 2.4)	78.2
6″	3.56 (dd, 12.0, 4.8)	62.6
	3.68 (dd, 12.0, 2.4)	

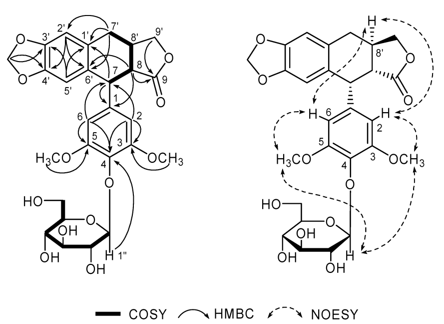

Fig. 2. Selected 2D NMR Spectral Data of **11**

lignans afforded the positive Cotton effect around 280—290 nm, while 7β-aryl (=7*S*) derivatives showed the negative Cotton curve in the CD spectrum.[17,18] Consequently, **11** showed a positive Cotton effect at 288 nm and hence, the absolute configuration at C-7 was determined to be *R*. The large coupling constant between H-8 and H-8′ (J=13.8 Hz) as well as the NOESY correlations between H-2, H-6 and H-8′ (Fig. 2) indicated the H-8/H-8′ *trans*-configuration. Therefore, the absolute configurations of C-8 and C-8′ were assigned as both *R*. Based on the evidence, the structure of **11** was determined to be (7*R*,8*R*,8′*R*)-4-demethyldeoxypodophyllotoxin 4-*O*-β-D-glucopyranoside. Up to now, 4-demethyldeoxypodophyllotoxin 4-*O*-glucopyranoside, having the same planar structure as the aglycone part in **11**, have already been isolated from *Podophyllum emodi*,[19] *P. peltatum*,[19] and *P. versipelle*.[20] However, in these papers, unambiguous structural determination procedures were not discussed and hence the absolute structure of **11** is represented here for the first time.

Table 3. ^{1}H- (600 MHz) and ^{13}C-NMR (150 MHz) Spectral Data of **12** and **14** in MeOH-d_4

No.	12		14	
	δ_H	δ_C	δ_H	δ_C
2	5.46 (d, 6.6)	89.5	5.49 (d, 6.3)	89.1
3	3.63 (m)	52.8	3.47 (br q, 6.3)	55.5
3a	3.89 (dd, 9.7, 7.6)	70.2[a]	3.83 (dd, 11.1, 5.5)	65.1
	3.72 (dd, 9.7, 5.3)		3.76 (dd, 11.1, 7.3)	
4	6.70 (br s)	117.7	6.75 (br s)	118.2[b]
4a		129.5		129.9
5		137.0		136.9
5a	2.63 (t, 7.3)	32.9	2.68 (t, 7.8)	33.0
5b	1.82 (tt, 7.3, 6.6)	35.7	1.90 (br quint, 6.6)	33.0
5c	3.56 (t, 6.6)	62.2	3.92 (dt, 9.6, 6.3)	70.0
			3.53 (dt, 9.6, 6.3)	
6	6.73 (br s)	114.3	6.75 (br s)	114.3[b]
7		145.2		145.3
7a		147.5[c]		147.6
1′		134.5		134.9
2′	6.94 (d, 1.8)	110.5	6.95 (d, 1.8)	110.6
3′		149.1		149.2
4′		147.6[c]		147.6
5′	6.78 (d, 8.1)	116.2	6.76 (d, 8.1)	116.2
6′	6.82 (dd, 8.1, 1.8)	119.8	6.82 (dd, 8.1, 1.8)	119.8
7-OCH_3	3.85 (s)	56.8	3.85 (s)	56.9
3′-OCH_3	3.82 (s)	56.5	3.81 (s)	56.4
Rha 1″	4.73 (d, 1.6)	101.7		
2″	3.81 (dd, 3.3, 1.6)	72.2		
3″	3.59 (dd, 9.6, 3.3)	72.5		
4″	3.37 (dd, 9.6, 9.3)	73.8		
5″	3.52 (dd, 9.3, 6.3)	70.3[a]		
6″	1.25 (d, 6.3)	18.0		
Glc 1‴			4.25 (d, 7.8)	104.6
2‴			3.20 (dd, 7.8, 9.0)	75.3
3‴			3.35 (dd, 9.0, 9.0)	78.2
4‴			3.29 (dd, 9.0, 9.0)	71.8
5‴			3.25 (ddd, 9.0, 5.5, 2.3)	78.0
6‴			3.85 (dd, 11.8, 2.3)	62.9
			3.66 (dd, 11.8, 5.5)	

a)—*c)* Assignments are interchangeable.

Compound **12**, a white amorphous powder, gave a molecular formula of $C_{26}H_{34}O_{10}$ based on the $[M-H]^-$ ion peak at m/z 505.2073 in the negative ion HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectra suggested that **12** was a dihydrobenzofuran-type neolignan glycoside carrying an α-L-rhamnopyranosyl moiety as a sugar part (Table 3). The structure of the aglycone in **12** was elucidated from ^{1}H–^{1}H COSY and HMBC experiments (Fig. 3). The relative configurations of H-2 and H-3 were determined to be *trans* based on the NOESY correlations (H-2/H_2-3a and H-3/H-2′, H-6′) (Fig. 3). The positive Cotton effect at 241 nm in the CD spectrum assigned the absolute stereochemistries of C-2 and C-3 to be *S* and *R*, respectively.[15] In conclusion, the structure of **12** is determined to be (2*S*,3*R*)-2,3-dihydro-3-hydroxymethyl-7-methoxy-2-(4′-hydroxy-3′-methoxyphenyl)-5-benzofuranpropanol 3a-*O*-α-L-rhamnopyranoside. Dihydrobenzofuran-type neolignan rhamnosides, having the same plane structure as the aglycone part in **12**, have already been isolated from *Pinus massoniana*,[21] *Baseonema acuminatum*,[22] and *Junipe-*

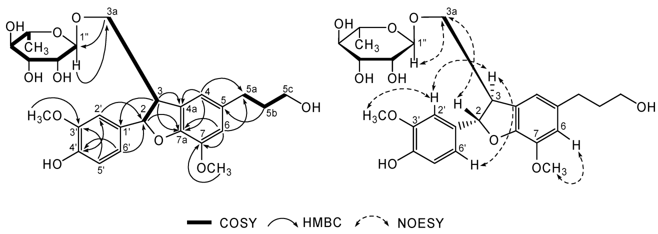

Fig. 3. Selected 2D NMR Spectral Data of **12**

rus polycarpus.[23)] However, in these papers, the absolute configurations on the dihydrobenzofuran ring were not discussed and hence the absolute structure of **12** based on CD analyses is represented here for the first time.

Compound **14**, a white amorphous powder, had the molecular formula $C_{26}H_{34}O_{11}$, which was determined based on the $[M-H]^-$ ion at *m/z* 521.2038 in negative ion HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectral data exhibited the presence of a β-D-glucopyranosyl moiety as the sugar part. In addition the ^{1}H- and ^{13}C-NMR spectral data of the aglycone of **14** was almost same with those of **12** (Table 3). The CD Cotton curve of **14** was opposite to that of **12**, suggesting that the aglycone of **14** was the enantiomer of the aglycone of **12**. On the basis of the above evidence as well as the precise spectroscopic analyses, the structure of **14** was determined to be (2*R*,3*S*)-2,3-dihydro-3-hydroxymethyl-7-methoxy-2-(4′-hydroxy-3′-methoxyphenyl)-5-benzo-furanpropanol 5c-*O*-β-D-glucopyranoside. Calis *et al.* reported the isolation of a dihydrobenzofuran-type neolignan glucoside having the same structure as **14** from *Phlomis viscose*.[24)] However, no chemical and spectral data of this compound were provided in the report. Thus the ^{1}H- and ^{13}C-NMR assignments in Table 3 and other physical properties in the experimental are reported here for the first time.

Experimental

^{1}H- and ^{13}C-NMR spectra were measured on a JEOL JNM-ECA 600 (^{1}H at 600 MHz and ^{13}C at 150 MHz) or JEOL JNM-GX 400 (^{1}H at 400 MHz and ^{13}C at 100 MHz) spectrometer. Chemical shifts are given in δ values (ppm) relative to tetramethylsilane (TMS) as an internal standard. FAB- and HR-FAB-MS spectra in negative mode (matrix, triethanolamine) were obtained with a JEOL JMS-700T spectrometer. Optical rotations were recorded on a JASCO P-1020 polarimeter and CD spectra on a JASCO J-805 spectropolarimeter, respectively. IR and UV spectra were measured on JASCO FT/IR-410 and Shimadzu UV-1600 UV/VIS spectrophotometers, respectively. For column chromatography, silica gel 60 (230—400 mesh, Merck), Chromatorex ODS DM1020T (100—200 mesh, Fuji Silysia), and Sephadex LH-20 (Amersham Biosciences) were used. Kiesel gel 60 F_{254} (Merck) and RP-18 F_{254} (Merck) were used for analytical TLC. Preparative HPLC was performed on a JAI LC-918 instrument with an RI-50 differential refractometer and a JAIGEL-ODS or a JAIGEL-GS 310 column, and also on a JASCO PU-2086 instrument with an RI-2031 differential refractometer and a TSK gel ODS-80 T_S column.

Plant Material The leaves and stems of *J. communis* var. *depressa* were collected in July 1997, in Oregon, U.S.A. A voucher specimen (Murata *et al.*, No. 053) was deposited in the Herbarium, Botanical Gardens, The University of Tokyo (TI), Japan.

Extraction and Isolation The dried and cut materials (2.4 kg) were extracted three times with MeOH (18 l×weekly) at room temperature. The MeOH solution was evaporated *in vacuo* to afford a dark greenish extract (488 g), an aliquot (202 g) of which was partitioned between *n*-hexane and MeOH. The MeOH-soluble part (130 g) was further partitioned between *n*-BuOH and water. The resulting *n*-BuOH extract (76 g) was chromatographed on silica gel and eluted with $CHCl_3$–MeOH–H_2O (7 : 3 : 1, a lower phase) to give 10 fractions (for each fraction, the abbreviations from A to J are used). Fraction D (1.32 g) was divided into 5 subfractions (from D-1 to D-5) with a Sephadex LH-20 column eluted with MeOH. Fraction D-2 was purified by repeated HPLC separation using JAIGEL-GS column (eluted with 50% MeOH) to give **11** (12.0 mg) and another crude fraction. The crude fraction was further purified with HPLC (JAIGEL-ODS; eluted with 60% MeOH) to give **8** (0.9 mg). Fraction E (4.21 g) was divided into two subfractions (E-1 and E-2) with a Sephadex LH-20 column eluted with acetone. Fraction E-2 was separated with Sephadex LH 20 column chromatography (eluted with 70% Acetone) into four subfractions. Subfraction 2 was applied to ODS column chromatography eluted with 60% MeOH to afford six fractions. The sixth fraction was further purified with HPLC (JAIGEL-ODS; eluted with 50% MeOH) to give **12** (8.3 mg). Subfraction 4 was further purified with HPLC (JAIGEL-GS; eluted with 60% MeOH) to give **16** (6.4 mg). Fraction F (6.2 g) was subsequently fractionated with silica gel column chromatography [$CHCl_3$–MeOH–H_2O (9 : 3 : 1, a lower phase)] into two subfractions (F-1 and F-2). Fraction F-2 was separated with Sephadex LH-20 column chromatography (eluted with MeOH) followed by ODS column chromatography (eluted with 50% MeOH) to afford three subfractions. Subfraction 1 was further purified with HPLC (JAIGEL-GS; eluted with MeOH) to give **7** (3.8 mg) and **9** (3.8 mg). Subfraction 3 was further purified with HPLC (JAIGEL-GS; eluted with 50% MeOH) to give **5** (3.3 mg). The fraction G (8.8 g) was applied onto a Sephadex LH-20 column (eluted with MeOH) followed by ODS column chromatography (eluted successively with 50% MeOH, 70% MeOH and MeOH) to divide five subfractions (from G-1 to G-5). Fraction G-3 was separated with ODS column chromatography (eluted with 50% MeOH) into four subfractions. Subfraction 3 was applied to ODS column chromatography (eluted with 40% MeOH) and HPLC (JAIGEL-GS; eluted with 50% MeOH) to afford four subfractions. The second fraction was further purified with HPLC (TSK gel ODS-80 T_S; eluted with 50% MeOH) to give **2** (23.3 mg). The fourth fraction was further purified with HPLC (TSK gel ODS-80 T_S; eluted with 50% MeOH), followed by HPLC (JAIGEL-GS; eluted with 50% MeOH) to afford **14** (1.8 mg). Subfraction 4 was further purified with HPLC (JAIGEL-ODS; eluted with 50% MeOH) to give **15** (6.4 mg). Fraction G-5 was subjected to ODS column chromatography (eluted with 50% MeOH) to separate three subfractions. Subfraction 1 was further purified by HPLC (JAIGEL-ODS; eluted with 50% MeOH) to give **4** (2.4 mg). Fraction H (10.8 g) was divided into 13 fractions (from H-1 to H-13) with ODS column chromatography eluted with 50% MeOH. Fraction H-8 was purified by ODS column chromatography (eluted with 50% MeOH) to be divided into six subfractions. Subfraction 4 was further purified by HPLC (JAIGEL-GS; eluted with 50% MeOH) to give **1** (14.5 mg). Fraction H-9 was subsequently fractionated with silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 1, a lower phase)] into four subfractions. Subfraction 1 was divided into two fractions with ODS column chromatography eluted with 15% MeOH. The latter fraction was further purified by HPLC (TSK gel ODS-80 T_S; eluted with 15% MeOH) to give **6** (22.3 mg). Subfraction 2 was subjected to ODS column chromatography eluted with 30% MeOH, followed by HPLC (TSK gel ODS-80 T_S; eluted with 15% MeOH) to afford **3** (17.8 mg) and **10** (4.0 mg). Subfraction 3 was divided into three fractions with HPLC (JAIGEL-GS; eluted with 50% MeOH) and the resulting second fraction was purified by HPLC (TSK gel ODS-80 T_S; eluted with 40% MeOH) to give **13** (7.2 mg).

Junipediol B 8-*O*-(6′-*O*-α-L-arabinofuranosyl)-β-D-glucopyranoside (**1**): A white amorphous powder, $[\alpha]_D$ −18.9° (c=0.40, MeOH). HR-FAB-MS (negative mode) *m/z*: 489.1604 $[M-H]^-$ (Calcd for $C_{21}H_{29}O_{13}$, 489.1608). IR (film) cm^{-1}: 3350, 2924, 1069, 1038. UV λ_{max} (MeOH) nm (log ε): 204 (4.30), 228 (sh, 3.73), 284 (3.50). ^{1}H- and ^{13}C-NMR data are given in Table 1.

cis-Cinnamyl Alcohol 9-*O*-(6′-*O*-α-L-arabinofuranosyl)-β-D-glucopyranoside (**4**): A white amorphous powder, $[\alpha]_D$ −70.1° (c=0.89, MeOH). FAB- and HR-FAB-MS (negative mode) *m/z*: 427.1615 $[M-H]^-$ (Calcd for $C_{20}H_{27}O_{10}$, 427.1604), 295 $[M-H-Ara\ (f)]^-$. IR (film) cm^{-1}: 3358, 2926, 1069, 1041. UV λ_{max} (MeOH) nm (log ε): 207 (4.21), 244 (3.98). ^{1}H- and ^{13}C-NMR data are given in Table 1.

(7*R*,8*R*,8′*R*)-4-Demethyldeoxypodophyllotoxin 4-*O*-β-D-glucopyranoside (**11**): A white amorphous powder, $[\alpha]_D$ −45.7° (c=0.47, MeOH). FAB- and HR-FAB-MS (negative mode) *m/z*: 545.1667 $[M-H]^-$ (Calcd for $C_{27}H_{29}O_{12}$, 545.1659), 383 $[M-H-162]^-$. IR (film) cm^{-1}: 3375, 2923, 1767, 1592, 1485, 1227, 1122, 1037. UV λ_{max} (MeOH) nm (log ε): 214 (4.36), 230 (sh, 4.13), 290 (3.62). CD (c=9.90×10^{-5} mol/l, MeOH) $\Delta\varepsilon$ (λ nm): −1.42 (277), +0.23 (288). ^{1}H- and ^{13}C-NMR data are given in Table 2.

(2*S*,3*R*)-2,3-Dihydro-3-hydroxymethyl-7-methoxy-2-(4′-hydroxy-3′-methoxyphenyl)-5-benzofuranpropanol 3a-*O*-α-L-rhamnopyranoside (**12**): A white amorphous powder, $[\alpha]_D$ −4.50° (c=0.31, MeOH). HR-FAB-MS (negative mode) *m/z*: 505.2073 $[M-H]^-$ (Calcd for $C_{26}H_{33}O_{10}$, 505.2074). IR (film) cm^{-1}: 3363, 2932, 1604, 1517, 1456, 1274, 1213, 1139, 1048. UV

λ_{max} (MeOH) nm (log ε): 210 (4.48), 225 (sh, 4.20), 282 (3.85). CD (c=7.95$\times10^{-5}$ mol/l, MeOH) $\Delta\varepsilon$ (λ nm): +5.25 (210), +0.36 (225), +1.88 (241), +1.05 (291). ^{1}H- and ^{13}C-NMR data are given in Table 3.

(2*R*,3*S*)-2,3-Dihydro-3-hydroxymethyl-7-methoxy-2-(4′-hydroxy-3′-methoxyphenyl)-5-benzofuranpropanol 5c-*O*-β-D-glucopyranoside (**14**): A white amorphous powder, $[\alpha]_D$ −12.4° (c=0.18, MeOH). HR-FAB-MS (negative mode) *m/z*: 521.2038 $[M-H]^-$ (Calcd for $C_{26}H_{33}O_{11}$, 521.2023). IR (film) cm^{-1}: 3365, 2936, 1605, 1518, 1455, 1276, 1212, 1030. UV λ_{max} (MeOH) nm (log ε): 210 (4.54), 226 (sh, 4.21), 282 (3.80). CD (c=6.90$\times10^{-5}$ mol/l, MeOH) $\Delta\varepsilon$ (λ nm); −3.69 (211), +0.23 (225), −1.19 (243), −0.54 (294). ^{1}H- and ^{13}C-NMR data are given in Table 3.

Acid Hydrolysis of Compounds 1, 4, 11, 12, and 14 Each glycoside (*ca.* 1 mg) in 1 M HCl (1.0 ml) was heated at 95 °C for 3 h. After cooling, the reaction mixture was neutralized with Amberlite IRA-93ZU (Organo Co., Ltd., Tokyo, Japan) and passed through an OASIS HLB cartridge column. The solution was concentrated to give a sugar fraction, which was analyzed by HPLC under the following conditions: column, COSMOSIL Sugar-D (4.6 mm i.d.×250 mm, Nacalai Tesque Inc., Kyoto, Japan); solvent, CH_3CN–H_2O (4 : 1); flow rate, 1.0 ml/min; detection, optical rotation, JASCO OR-2090 Plus. Identification of D-glucose (from **1**, **4**, **11**, and **14**), L-arabinose (from **1** and **4**), and L-rhamnose (from **12**) present in the sugar fraction was carried out by comparison of their retention times (t_R) and optical rotations with those of authentic samples. t_R (min): 11.6 (D-glucose, positive optical rotation), 8.6 (L-arabinose, positive optical rotation), 6.9 (L-rhamnose, negative optical rotation).

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