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Six new flavonolignans from *Sasa veitchii* (Carr.) Rehder

Yuki Nakajima, Young Sook Yun and Akira Kunugi*

Graduate School of Life Science, Tokyo University of Pharmacy and Life Science, 1432-1 Horinouchi, Hachioji, Tokyo 192-0392, Japan

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Abstract—From dry leaves of *Sasa veitchii* (Carr.) Rehder, six new flavonolignans **4**–**9**, each consisting of a tricin unit linked to a guaiacylglyceryl derivative were isolated and their structures were determined on the basis of spectroscopic data and chemical evidence. These flavonolignans were found to be three pairs of stereoisomers.

1. Introduction

Dry leaves of *Sasa veitchii* (Carr.) Rehder (called Kumazasa in Japan) have been used for a long time in Asia as health food and in folk medicine, and recently, are used as a dietary and/or food supplement in Japan. It is reported that the leaves have various biological activities including anti-ulcer,[1,2] anti-inflammatory,[1] sedative,[2] detoxicating,[2] diuretic,[2] hypotensive,[3] anti-tumor,[4–6] and antimicrobial[7] activities. However, scarcely any chemical investigation has been made on the plant.

In the present work, we conducted chemical studies on Kumazasa to identify the effective constituents in this plant, and isolated six new compounds **4**–**9** along with three known flavonoids, i.e. tricin (**1**), tricin 4′-*O*-(*threo*-β-guaiacylglyceryl) ether (**2**) and tricin 4′-*O*-(*erythro*-β-guaiacylglyceryl) ether (**3**). Compounds **4**–**9** were new flavonolignans consisting of a tricin unit linked to a guaiacylglyceryl derivative, and their structures were determined on the basis of the spectroscopic data including 2D NMR spectra and chemical evidence. Those compounds **2**–**9**, having two chiral centers at 7″ and 8″, are in fact four pairs of stereoisomers. We studied on the configuration of **2**, **3**, **8** and **9**, and found that **2** and **3**, and **8** and **9** were stereoisomers at 7″.

2. Results and discussion

By HP-20 column chromatography, and subsequent silica gel and ODS column chromatography, the ethyl acetate-soluble portion (105.66 g) of the 80% methanolic extract (1.7 kg) derived from dry leaves of Kumazasa, *S. veitchii* (Carr.) Rehder (20 kg), gave a flavone **1** and eight flavonolignans **2**–**9**.

Of them, **1**–**3** were identified as known compounds, by studying their mass, UV and NMR spectral data and by the comparison of the data with those in the literature. Thus, **1** was shown to be tricin,[8] **2** to be tricin 4′-*O*-(*threo*-β-guaiacylglyceryl) ether and **3** to be tricin 4′-*O*-(*erythro*-β-guaiacylglyceryl) ether.[9,10] Compounds **2** and **3**, having the same gross structure and different physical properties, are known to be stereoisomers due to the presence of two adjacent chiral centers at C-7″ and C-8″.[11] In the present study, by reduction of 7″-OH with Et_3SiH,[12] **2** and **3** gave an identical reduction product **10** and demonstrated that **2** and **3** were the epimers whose configurations at 7″ were different.

Compounds **4** and **5**, both yellow amorphous solid of the molecular formula $C_{29}H_{28}O_{12}$, exhibited UV absorption maxima at 310 and 322 nm, respectively, implying the presence of a highly conjugated double bond system in the molecule. Their IR spectra showed the presence of OH groups (3407 cm^{-1} for **4** and 3388 cm^{-1} for **5**), and aromatic rings (1615 and 1592 cm^{-1} for **4** and 1614 and 1591 cm^{-1} for **5**), and ^1H NMR spectra showed the signals for eight aromatic ring protons (δ 6.22, 6.48, 6.71, 6.75, 6.87, 7.03, and 7.23×2 for **4** and δ 6.20, 6.46, 6.68, 6.75, 6.83, 7.01, and 7.19×2 for **5**), three methoxy groups (δ 3.85 and 3.93×2 for **4** and δ 3.84 and 3.90×2 for **5**), an acetyl group (δ 1.90 for **4** and δ 1.89 for **5**), and four methine or methylene protons (δ 3.96, 4.29, 4.57, and 4.94 for **4** and δ 4.28, 4.42, 4.67, and 4.93 for **5**). The ^{13}C NMR spectra had signals caused by a conjugated ketonic carbon (δ 184.0 for **4** and δ 183.8 for **5**), 20 aromatic or olefinic carbonds (δ 95–167), three methoxy groups (δ 56.6 and 57.1×2 for **4** and δ 56.4 and 56.9×2 for **5**), an acetyl group (δ 20.8 and 172.7 for **4** and δ 20.7 and 172.7 for **5**), and two oxygenated methine carbons (δ 75.2 and 85.6 for **4** and δ 74.1 and 84.5 for **5**), and one oxygenated methylene carbon (δ 65.5 for **4** and δ 64.7

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* Corresponding author. Tel.: +81-426-76-5319; fax: +81-426-76-9412; e-mail: kunugi@ls.toyaku.ac.jp

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Table 1. Chemical shift (δ) of ^{1}H NMR signals of compounds **2**–**11**

	2[a]	**3**[a]	**4**[b]	**5**[b]	**6**[b]
3	6.71 (1H, s)	6.70 (1H, s)	6.71 (1H, s)	6.68 (1H, s)	6.70 (1H, s)
6	6.21 (1H, d, 2.1)	6.21 (1H, d, 2.0)	6.22 (1H, d, 1.8)	6.20 (1H, d, 1.2)	6.21 (1H, d, 1.7)
8	6.46 (1H, d, 2.1)	6.47 (1H, d, 2.0)	6.48 (1H, d, 1.8)	6.46 (1H, d, 1.2)	6.48 (1H, d, 1.7)
2′,6′	7.26 (2H, s)	7.24 (2H, s)	7.23 (2H, s)	7.19 (2H, s)	7.23 (2H, s)
2″	7.02 (1H, d, 1.8)	6.99 (1H, d, 1.8)	7.03 (1H, d, 1.5)	7.01 (1H, d, 1.5)	6.95 (1H, d, 1.5)
5″	6.75 (1H, d, 8.0)	6.73 (1H, d, 8.0)	6.75 (1H, d, 8.1)	6.75 (1H, d, 8.1)	6.79 (1H, d, 8.1)
6″	6.88 (1H, dd, 1.8, 8.0)	6.82 (1H, dd, 1.8, 8.0)	6.87 (1H, dd, 1.5, 8.1)	6.83 (1H, dd, 1.5, 8.1)	6.82 (1H, dd, 1.5, 8.1)
7″	5.01 (1H, d, 6.5)	4.91 (1H, d, 5.4)	4.94 (1H, d, 6.2)	4.93 (1H, d, 4.9)	4.50 (1H, d, 6.6)
8″	4.31 (1H, ddd, 3.8, 4.0, 6.5)	4.46 (1H, ddd, 3.4, 4.0, 5.4)	4.57 (1H, ddd, 3.3, 5.1, 6.2)	4.67 (1H, ddd, 3.1, 4.9, 6.5)	4.68 (1H, ddd, 3.2, 6.3, 6.6)
9″	3.42 (1H, dd, 3.8, 12.1)	3.69 (1H, dd, 3.4, 12.1)	3.96 (1H, dd, 5.1, 11.9)	4.28 (1H, dd, 3.1, 11.9)	3.88 (1H, dd, 6.3, 11.9)
	3.81 (1H, dd, 4.0, 12.1)	3.94 (1H, dd, 4.0, 12.1)	4.29 (1H, dd, 3.3, 11.9)	4.42 (1H, dd, 6.5, 11.9)	4.17 (1H, dd, 3.2, 11.9)
2‴,6‴					
3‴,5‴					
7‴					
8‴					
3′,5′OMe	3.95 (6H, s)	3.92 (6H, s)	3.93 (6H, s)	3.90 (6H, s)	3.91 (6H, s)
3″OMe	3.84 (3H, s)	3.83 (3H, s)	3.85 (3H, s)	3.84 (3H, s)	3.85 (3H, s)
7″OMe					3.21 (3H, s)
9″OAc			1.90 (3H, s)	1.89 (3H, s)	1.93 (3H, s)

	7[b]	**8**[b]	**9**[b]	**10**[b]	**11**[b]
3	6.67 (1H, s)	6.57 (1H, s)	6.60 (1H, s)	6.65 (1H, s)	6.61 (1H, s)
6	6.21 (1H, d, 2.0)	6.20 (1H, d, 1.9)	6.21 (1H, d, 1.9)	6.21 (1H, d, 1.9)	6.21 (1H, d, 2.0)
8	6.46 (1H, d, 2.0)	6.37 (1H, d, 1.9)	6.39 (1H, d, 1.9)	6.48 (1H, d, 1.9)	6.40 (1H, d, 2.0)
2′,6′	7.16 (2H, s)	7.16 (2H, s)	7.20 (2H, s)	7.23 (2H, s)	7.20 (2H, s)
2″	6.92 (1H, d, 1.5)	7.09 (1H, d, 1.8)	7.10 (1H, d, 1.7)	6.71 (1H, *)	6.92 (1H, brs)
5″	6.76 (1H, d, 8.1)	6.80 (1H, d, 8.1)	6.80 (1H, d, 8.1)	6.70 (1H, d, 8.1)	6.75 (1H, brs)
6″	6.78 (1H, dd, 1.5, 8.1)	6.93 (1H, dd, 1.8, 8.1)	6.90 (1H, dd, 1.7, 8.1)	6.67 (1H, dd, 1.7, 8.1)	6.75 (1H, brs)
7″	4.45 (1H, d, 5.6)	4.98 (1H, d, 6.0)	5.00 (1H, d, 4.9)	2.96 (2H, m)	2.98 (1H, dd, 6.9, 14.0)
					3.11 (1H, dd, 6.3, 14.0)
8″	4.67 (1H, m)	4.74 (1H, m)	4.81 (1H, *)	4.44 (1H, m)	4.83 (1H, m)
9″	4.34 (1H, dd, 2.8, 11.9)	4.22 (1H, dd, 6.4, 11.9)	4.36 (1H, dd, 2.3, 11.9)	3.59 (1H, dd, 4.5, 11.8)	4.21 (1H, dd, 2.6, 11.7)
	4.41 (1H, dd, 6.2, 11.9)	4.24 (1H, dd, 2.8, 11.9)	4.55 (1H, dd, 7.7, 11.9)	3.63 (1H, dd, 3.3, 11.8)	4.31 (1H, dd, 7.1, 11.7)
2‴,6‴		6.61 (2H, d, 8.6)	6.60 (2H, d, 8.6)		6.63 (2H, d, 8.6)
3‴,5‴		7.25 (2H, d, 8.6)	7.23 (2H, d, 8.6)		7.27 (2H, d, 8.6)
7‴		7.09 (1H, d, 15.9)	7.04 (1H, d, 16.0)		7.13 (1H, d, 16.0)
8‴		6.03 (1H, d, 15.9)	6.01 (1H, d, 16.0)		6.08 (1H, d, 16.0)
3′,5′OMe	3.87 (6H, s)	3.88 (6H, s)	3.90 (6H, s)	3.91 (6H, s)	3.88 (6H, s)
3″OMe	3.83 (3H, s)	3.86 (3H, s)	3.88 (3H, s)	3.82 (3H, s)	3.85 (3H, s)
7″OMe	3.28 (3H, s)				
9″OAc	1.92 (3H, s)				

J-values are given in Hz in parentheses. *Multiplicity was not determined due to overlapping of the signals.
[a] Data were recorded at 400 MHz.
[b] Data were recorded at 500 MHz.

for **5**). The ^{1}H and ^{13}C NMR spectra of **4** and **5** were quite similar to those of **2** and **3**, and the basic structures of **4** and **5** were thus determined to be 5,7,4′-trihydroxy-3′,5′-dimethoxyflavone (tricin) linked to acetylguaiacylglycerol. The acetoxy group was shown to be at C-9″, as an HMBC spectral correlation was observed between the acetyl carbonyl carbon at δ 172.7 and one of the methylene protons of guaiacylglyceryl moiety at δ 3.96 for **4** and the corresponding ones between the acetyl carbonyl carbon at δ 172.7 and the methylene protons (H_2-9″) of guaiacylglycerol moiety at δ 4.28 and 4.42 for **5**. In the ^{1}H NMR spectra, the coupling constant between the adjacent protons of *threo* type is known to be larger (5.0–8.2 Hz) than that of *erythro* type (4.5–5.4 Hz).[10] As in the case of **2** and **3**, **4** and **5** were identified as diastereomers, the coupling constant $J_{\text{H-7}'',\ \text{H-8}''}$ of **4** being 6.2 Hz and that of **5** 4.9 Hz. The corresponding *J* values of compounds **4** and **5** in a 3:1 mixture of $CDCl_3/CD_3OD$ were 8.0 and 6.0 Hz, respectively. Thus the structure of **4** was determined to be tricin 4′-*O*-[*threo*-β-guaiacyl-(9″-*O*-acetyl)-glyceryl] ether, and that of **5** was tricin 4′-*O*-[*erythro*-β-guaiacyl-(9″-*O*-acetyl)-glyceryl] ether.

Compounds **6** and **7** were both yellow amorphous solid of the molecular formula $C_{30}H_{30}O_{12}$. As shown in Section 3, the UV, IR, ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2) spectral features of **6** and **7** were generally similar to those of **2**–**5**, implying that **6** and **7** were also flavonolignans of the same basic structures as **2**–**5** and having four methoxy groups. A long-range coupling was observed between the methoxy protons (δ 3.21 for **6** and 3.28 ppm for **7**) and C-7″ (δ 85.6 for **6** and δ 84.4 for **7**) in their HMBC spectra to show that the methoxy group was located at C-7″. The difference in the physical features between **6** and **7** suggested that they were diastereomers as in **2** and **3** or **4** and **5**. The coupling constant of $J_{\text{H-7}'',\ \text{H-8}''}$ was 6.6 Hz for **6** and 5.6 Hz for **7**, and the corresponding *J* values of compounds **6** and **7** in a 3:1 mixture of $CDCl_3/CD_3OD$ were

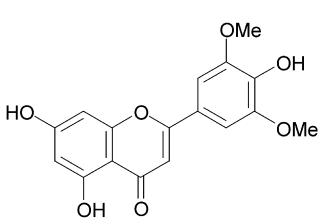
Table 2. Chemical shift (δ) of ^{13}C NMR signals of compounds **2**–**11**

	2[a]	**3**[a]	**4**[b]	**5**[b]	**6**[b]	**7**[b]	**8**[b]	**9**[b]	**10**[b]	**11**[b]
2	165.1	165.3	163.4	163.2	163.4	163.4	165.0	165.2	165.4	165.1
3	105.9	105.8	106.1	105.9	105.8	106.0	105.4	105.6	105.4	105.4
4	183.7	183.8	184.0	183.8	183.8	184.0	183.7	183.9	183.8	183.7
5	163.1	163.3	165.4	165.2	165.4	165.5	163.2	163.4	163.3	163.2
6	100.7	100.5	100.5	100.3	100.3	100.4	100.4	100.6	100.4	100.4
7	167.4	167.0	166.5	166.2	166.3	166.4	166.5	166.7	166.6	165.1
8	95.5	95.4	95.4	95.2	95.2	95.4	95.2	95.4	95.3	95.4
9	159.6	159.6	159.6	159.4	159.5	159.6	159.4	159.6	159.5	159.6
10	105.1	105.3	105.7	105.4	105.5	105.7	105.7	105.9	105.8	105.7
1′	128.1	127.9	128.2	127.9	127.5	127.9	126.7	127.0	127.8	126.7
2′,6′	105.1	105.2	105.2	105.0	105.0	105.1	105.0	105.1	105.2	105.0
3′,5′	154.7	154.9	154.9	154.8	154.8	154.8	154.8	155.0	155.2	155.0
4′	141.0	140.6	141.2	140.6	141.6	140.9	141.4	141.4	140.9	141.5
1″	133.2	133.9	133.2	133.4	130.5	130.9	133.2	133.9	131.0	133.2
2″	111.7	111.6	111.9	111.4	112.1	112.2	111.8	111.7	114.3	114.3
3″	148.7	148.7	147.6	147.0	147.8	147.7	147.4	147.3	146.0	146.3
4″	147.2	147.0	149.0	148.7	149.1	149.1	148.8	149.0	148.7	148.8
5″	115.8	115.6	116.1	115.7	116.1	116.0	115.9	116.0	116.0	116.1
6″	120.8	120.9	121.1	120.7	122.0	122.0	120.9	120.8	123.1	123.1
7″	74.4	74.3	75.2	74.1	85.6	84.4	75.1	74.8	38.3	38.9
8″	88.8	87.5	85.6	84.5	83.4	83.9	85.1	84.8	85.8	82.2
9″	62.1	62.0	65.5	64.7	65.5	65.1	66.5	66.0	63.9	67.9
1‴							127.7	127.8		127.6
2‴,6‴							131.2	131.2		131.1
3‴,5‴							116.7	116.9		116.7
4‴							161.3	161.4		161.3
7‴							146.5	146.5		146.5
8‴							114.5	114.9		114.6
9‴							168.6	168.9		168.7
3′,5′OMe	57.0	56.9	57.1	56.9	56.8	57.0	56.9	57.1	57.0	56.9
3′OMe	56.4	56.4	56.6	56.4	57.1	57.6	56.4	56.6	56.4	56.4
7″OMe					56.5	56.6				
9″OAc			172.7	172.7	172.5	172.9				
			20.8	20.7	20.7	20.9				

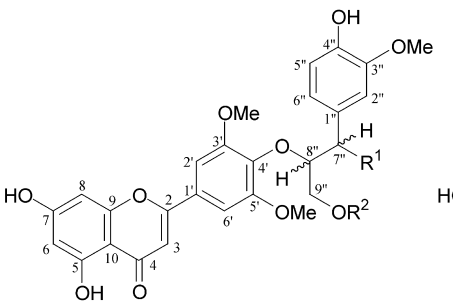
[a] Data were recorded at 100 MHz.
[b] Data were recorded at 125 MHz.

6.8 and 5.0 Hz, respectively, which revealed that **6** was of a *threo* type and **7** of an *erythro* type. Accordingly, the structures of **6** and **7** were determined to be tricin 4′-*O*-[*threo*-β-guaiacyl-(7″-*O*-methyl-9″-*O*-acetyl)-glyceryl] ether and tricin 4′-*O*-[*erythro*-β-guaiacyl-(7″-*O*-methyl-9″-*O*-acetyl)-glyceryl] ether, respectively.

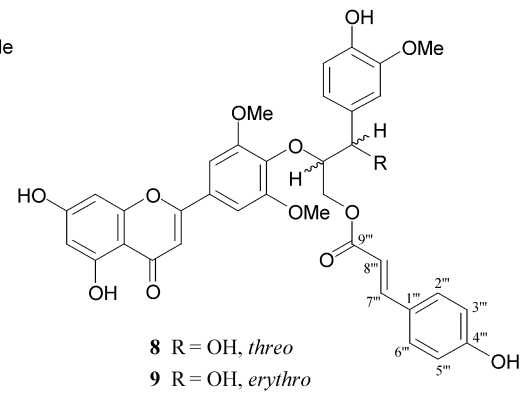
Compounds **8** and **9** were yellow amorphous solid of the molecular formula $C_{36}H_{32}O_{13}$. Their UV, IR, ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2) spectral profiles suggested that **8** and **9** were also flavonolignans, consisting of a tricin moiety, a guaiacylglyceryl group, and a *p*-coumaroyl group. The *p*-coumaroyl group was linked to the 9″ hydroxyl oxygen of the guaiacylglyceryl group as correlations in their HMBC spectra were observed between H_2-9″ of guaiacylglyceryl group and C-9‴ of the *p*-coumaroyl group.



1



2 R^1 = OH, R^2 = H, *threo*
3 R^1 = OH, R^2 = H, *erythro*
4 R^1 = OH, R^2 = Ac, *threo*
5 R^1 = OH, R^2 = Ac, *erythro*
6 R^1 = OMe, R^2 = Ac, *threo*
7 R^1 = OMe, R^2 = Ac, *erythro*
10 R^1 = R^2 = H



8 R = OH, *threo*
9 R = OH, *erythro*
11 R = H

Although **8** and **9** were of the same gross structure, the differences were clearly seen in the chemical shift and coupling constant parameters, as shown in Tables 1 and 2. The coupling constant of $J_{H\text{-}7'',\ H\text{-}8''}$ was 6.0 Hz for **8** and was 4.9 Hz for **9**, and the corresponding *J* values of compounds **8** and **9** in a 3:1 mixture of $CDCl_3/CD_3OD$ were 7.8 and 3.7 Hz, respectively, which revealed that **8** was of *threo* type and **9** of *erythro* type. Compounds **8** and **9** produced an identical reduction product when 7″-OH was reduced to H, as in the case of **2** and **3** to demonstrate that they were stereoisomers at 7″. Therefore, the structures of **8** and **9** were decided to be tricin 4′-*O*-[*threo*-β-guaiacyl-(9″-*O*-*p*-coumaroyl)-glyceryl] ether and tricin 4′-*O*-[*erythro*-β-guaiacyl-(9″-*O*-*p*-coumaroyl)-glyceryl] ether, respectively.

The flavonolignans have been separated from the Chenopodiaceae,[9] Gramineae,[10] Compositae,[13,14] Flacourtiaceae,[15] Leguminosae,[16,17] Crassulaceae,[18] Scrophulariaceae,[19] and Labiatae[20] families, and most of those known flavonolignans are of hydnocarpin-type in which a *trans*-substituted 1,4-dioxane ring is formed between the flavonoid moiety and the guaiacylglyceryl moiety, as in silybin.

In the present study, from *S. veitchii* (Carr.) Rehder, we separated eight flavonolignans including six new ones. This is the second report on the isolation of flavonolignans from a plant of the Gramineae family. Those eight flavonolignans from *S. veitchii* have no *trans*-1,4-dioxane ring in them; the flavonoid moiety and guaiacylglyceryl unit are linked by an ether linkage, which is rather unusual. The stereoisomers of flavonolignans are often not easy to be separated into individual components.[21] In the case of the present flavonolignans, they were easily separated by HPLC into individual components to show that the eight flavonolignans were in fact four pairs of stereoisomers. Further, in two pairs of the four pairs of stereoisomers, it was demonstrated that they were epimers having different stereochemistry at 7″.

3. Experimental

3.1. General experimental procedures

UV spectra were obtained on a Hitachi U-2001 spectrophotometer, and IR spectra were recorded on a Jasco FT/IR-620 spectrophotometer. Optical rotations were measured on a Jasco DIP-360 digital polarimeter. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on Bruker DPX-400 and DRX-500 spectrometers in CD_3OD. Standard pulse sequences and parameters were used for the experiments. ^1H chemical shifts in CD_3OD were referenced to residual CD_2HOD (3.31 ppm); ^{13}C chemical shifts were referenced to the solvent (CD_3OD, 49.0 ppm). ESI-MS (positive mode) was obtained on a Micromass LCT Spectrometer. HPLC was carried out with a Shimadzu LC-10AT pump and a SPE-10Avp detector by using Mightysil RP-18 columns (for analytical HPLC, 250×4.6 mm i.d.; 5 μm particle size and for preparative HPLC, 250×20 mm i.d.; 5 μm particle size, Kanto Kagaku Co., Ltd).

3.2. Plant material and separation of individual flavonolignans

S. veitchii (Carr.) Rehder was harvested in July and August in 2001 in Nagano prefecture, Japan. The air-dried leaves (20 kg) of the plant were extracted with 80% aqueous MeOH at room temperature (3×36 L, a week each). After filtration and removal of the solvent by evaporation in vacuo, a residue (1.7 kg) was obtained, which was suspended in H_2O (5 L). Then the suspension was treated with *n*-hexane (3×1.5 L), EtOAc (3×1.5 L), and *n*-BuOH (3×1.5 L), successively, to afford, after removal of solvent, *n*-hexane-soluble (100.03 g), EtOAc-soluble (105.66 g), and *n*-BuOH-soluble (203.66 g) portions.

The EtOAc-soluble portion (105.66 g) was placed on a Diaion HP-20 column (100×10 cm) and eluted sequentially with 3 L each of MeOH/H_2O mixtures (3:7, 6:4, 8:2, 1:0), and EtOAc to give five fractions (frs. 1–5). Chromatography of fr. 3 over silica gel eluting with gradient mixtures of $CHCl_3$ and MeOH (60:1–6:4) afforded eight fractions (frs. 3A–3H). Fr. 3B was placed on an ODS column and eluted sequentially with MeOH–H_2O mixtures (55:45, 60:40, 75:25, and 100:0). The earlier eluate was subjected to HPLC eluting with 35% aqueous CH_3CN to give compounds **4** (15 mg) and **5** (7.2 mg). The later eluate of the ODS column chromatography was subjected to HPLC eluting with 42% aqueous CH_3CN to give compounds **6** (10 mg) and **7** (11 mg). Fr. 3C was separated into subfractions (frs. 3C-1–3C-13) by ODS open column chromatography with a gradient solvent system (MeOH/H_2O 1:1→1:0). Fr. 3C-5 gave tricin (**1**) (27.7 mg), compounds **2** (38.0 mg) and **3** (31.8 mg) when subjected to LH-20 column chromatography followed by HPLC eluting with 35% aqueous CH_3CN. Fr. 3C-8 afforded compounds **8** (41.4 mg) and **9** (40.3 mg) when separated by HPLC eluting with 35% aqueous CH_3CN.

3.3. Characteristics of each compound

3.3.1. Tricin 4′-*O*-[*threo*-β-guaiacyl-(9″-*O*-acetyl)-glyceryl] ether (4). Yellow amorphous solid; $C_{29}H_{28}O_{12}$; HRESIMS *m/z* 569.1714 $[M+H]^+$ (calcd for $C_{29}H_{29}O_{12}$ 569.1659); $[\alpha]_D^{20}=-48.5°$ (*c* 0.11, MeOH); IR (neat) ν_{max} (cm^{-1}) 3407, 2939, 1734, 1654, 1615, 1592, 1517, 1497, 1166, 1126; UV (MeOH) λ_{max} (nm) 310 (log ε 4.06). ^1H NMR and ^{13}C NMR data are given in Tables 1 and 2, respectively.

3.3.2. Tricin 4′-*O*-[*erythro*-β-guaiacyl-(9″-*O*-acetyl)-glyceryl] ether (5). Yellow amorphous solid; $C_{29}H_{28}O_{12}$; HRESIMS *m/z* 569.1798 $[M+H]^+$ (calcd for $C_{29}H_{29}O_{12}$ 569.1659); $[\alpha]_D^{20}=-70.0°$ (*c* 0.15, MeOH); IR (neat) ν_{max} (cm^{-1}) 3388, 2939, 1709, 1655, 1614, 1591, 1517, 1497, 1166, 1126; UV (MeOH) λ_{max} (nm) 322 (log ε 3.94). ^1H NMR and ^{13}C NMR data are given in Tables 1 and 2, respectively.

3.3.3. Tricin 4′-*O*-[*threo*-β-guaiacyl-(7″-*O*-methyl-9″-*O*-acetyl)-glyceryl] ether (6). Yellow amorphous solid; $C_{30}H_{30}O_{12}$; HRESIMS *m/z* 583.1833 $[M+H]^+$ (calcd for $C_{30}H_{31}O_{12}$ 583.1816); $[\alpha]_D^{20}=+5.8°$ (*c* 0.41, MeOH); IR (neat) ν_{max} (cm^{-1}) 3407, 2935, 1731, 1654, 1590, 1496,

1165, 1127; UV (MeOH) λ_{max} (nm) 322 (log ε 4.40), 272 (log ε 4.39). ^{1}H NMR and ^{13}C NMR data are given in Tables 1 and 2, respectively.

3.3.4. Tricin 4′-*O*-[*erythro*-β-guaiacyl-(7″-*O*-methyl-9″-*O*-acetyl)-glyceryl] ether (7). Yellow amorphous solid; $C_{30}H_{30}O_{12}$; HRESIMS *m/z* 583.1857 $[M+H]^+$ (calcd for $C_{30}H_{31}O_{12}$ 583.1816); $[\alpha]_D^{20}=-13.8°$ (*c* 0.25, MeOH); IR (neat) ν_{max} (cm^{-1}) 3408, 2936, 1737, 1652, 1612, 1591, 496, 1180, 1127; UV (MeOH) λ_{max} (nm) 335 (log ε 4.20), 271 (log ε 4.21). ^{1}H NMR and ^{13}C NMR data are given in Tables 1 and 2, respectively.

3.3.5. Tricin 4′-*O*-[*threo*-β-guaiacyl-(9″-*O*-*p*-coumaroyl)-glyceryl] ether (8). Yellow amorphous solid; $C_{36}H_{32}O_{13}$; HRESIMS *m/z* 695.1709 $[M+Na]^+$ (calcd for $C_{36}H_{32}O_{13}Na$ 695.1741); $[\alpha]_D^{20}=+52.1°$ (*c* 0.48, MeOH); IR (neat) ν_{max} (cm^{-1}) 3388, 2925, 1685, 1648, 1585, 1509, 1159; UV (MeOH) λ_{max} (nm) 312 (log ε 4.58). ^{1}H NMR and ^{13}C NMR data are given in Tables 1 and 2, respectively.

3.3.6. Tricin 4′-*O*-[*erythro*-β-guaiacyl-(9″-*O*-*p*-coumaroyl)-glyceryl] ether (9). Yellow amorphous solid; $C_{36}H_{32}O_{13}$; HRESIMS *m/z* 695.1774 $[M+Na]^+$ (calcd for $C_{36}H_{32}O_{13}Na$ 695.1741); $[\alpha]_D^{20}=-30.4°$ (*c* 1.28, dioxane); IR (neat) ν_{max} (cm^{-1}) 3388, 2925, 1733, 1691, 1648, 1587, 1514, 1160; UV (MeOH) λ_{max} (nm) 310 (log ε 4.57). ^{1}H NMR and ^{13}C NMR data are given in Tables 1 and 2, respectively.

3.4. Reduction of compounds 2, 3, 8, and 9

Compound **2** (4.2 mg) was treated with Et_3SiH (30 μL) in the presence of TFA (10 μL) as a catalyst in CH_2Cl_2 (0.3 mL) at room temperature overnight. The crude reduction product was purified by HPLC with 35% aqueous CH_3CN to yield **10** (2.4 mg) as a yellow amorphous solid: $C_{27}H_{26}O_{10}$; HRESIMS *m/z* 511.1632 $[M+H]^+$ (calcd for $C_{27}H_{27}O_{10}$ 511.1604); $[\alpha]_D^{20}=+32.7°$ (*c* 0.1, MeOH); UV (MeOH) λ_{max} (nm) 334 (log ε 3.95). ^{1}H NMR and ^{13}C NMR data are given in Tables 1 and 2, respectively.

Compound **3** (2.7 mg) was treated and purified by HPLC in the same way as above to yield a reduction product (0.9 mg): $[\alpha]_D^{20}=+24.3°$ (*c* 0.05, MeOH). By the comparison of their ^{1}H NMR, UV, and HRESI mass spectra, t_R of HPLC analysis and optical rotations, this compound was shown to be identical to **10** from **2**.

Compound **8** (1.8 mg) was treated with Et_3SiH in the same way as above and purified by HPLC with 40% aqueous CH_3CN to yield **11** (1.6 mg) as a yellow amorphous solid: $C_{36}H_{32}O_{12}$; HRESIMS *m/z* 657.1978 $[M+H]^+$ (calcd for $C_{33}H_{33}O_{12}$ 657.1972); $[\alpha]_D^{20}=+55.7°$ (*c* 0.67, MeOH). ^{1}H NMR and ^{13}C NMR data are given in Tables 1 and 2, respectively.

Compound **9** (3.5 mg) was treated and purified by HPLC in the same way as for **8** to yield a reduction product (2.5 mg): $[\alpha]_D^{20}=+50.7°$ (*c* 0.73, MeOH). By the comparison of their ^{1}H NMR and HRESI mass spectra, t_R of HPLC analysis and optical rotations, this compound was shown to be identical to **11** from **8**.

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