Flavonoid Glycosides from *Botrychium ternatum*

Tsutomu Warashina,*[a] Kaoru Umehara,[b] and Toshio Miyase[b]

[a] *Institute for Environmental Sciences, University of Shizuoka; and* [b] *School of Pharmaceutical Sciences, University of Shizuoka; 52–1 Yada, Suruga-ku, Shizuoka 422–8526, Japan.*

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The MeOH extract from dried whole *Botrychium ternatum* plants yielded 33 compounds, including seventeen new flavonoid glycosides and sixteen known compounds. The structures of new compounds were established using NMR spectroscopic analysis and chemical evidence.

Key words *Botrychium ternatum*; Ophiolossaceae; flavonoid glycoside; kaempferol; ternatumoside

Recently, plants in the Ophiolossaceaus family were reported to be effective in the cosmetic field, for example, skin moisturizing and lightning actions, improvement and protection of rough skin, and proliferation of skin fibroblasts.[1,2] *Botrychium ternatum* is one of the Ophiolossaceaus plants and distributed to the Honshu, Shikoku, and Kyushu Islands in Japan, the Korean Peninsula, and China. In Japan, this plant is called "Fuyunohanawarabi" and used to treat dizziness, headache, cough, and fever as a folk medicine. In the course of research to find the efficient agents in the cosmetic field from the Ophiolossaceaus family, we investigated the constituents of *B. ternatum* and their biological activities.

A MeOH extract from dried whole *B. ternatum* plants was suspended in water. The suspension was extracted with diethyl ether and partitioned into an ether-soluble fraction and a H_2O-soluble fraction. The ether-soluble fraction was then separated into a *n*-hexane-soluble fraction and a MeOH–H_2O (9 : 1)-soluble fraction. The residue of the water soluble-fraction and the MeOH–H_2O (9 : 1)-soluble fraction was subjected to both silica gel column chromatography and semi-preparative HPLC to give thirty flavonoid glycosides (**1**–**30**), two flavonoids (**31**, **32**), and a bibenzyl derivative (**33**). Compounds **1**,[3] **2**,[4] **3**,[5] **5**,[5] **7**,[6] **13**,[7] **14**,[8] **15**,[9] **16**,[10] **17**,[11] **21**,[12] **24**,[13] **25**,[13] **31**,[14] **32**,[14] and **33**[15] were identified as shown in Chart 1 based on the ^{1}H- and/or ^{13}C-NMR spectroscopic data.

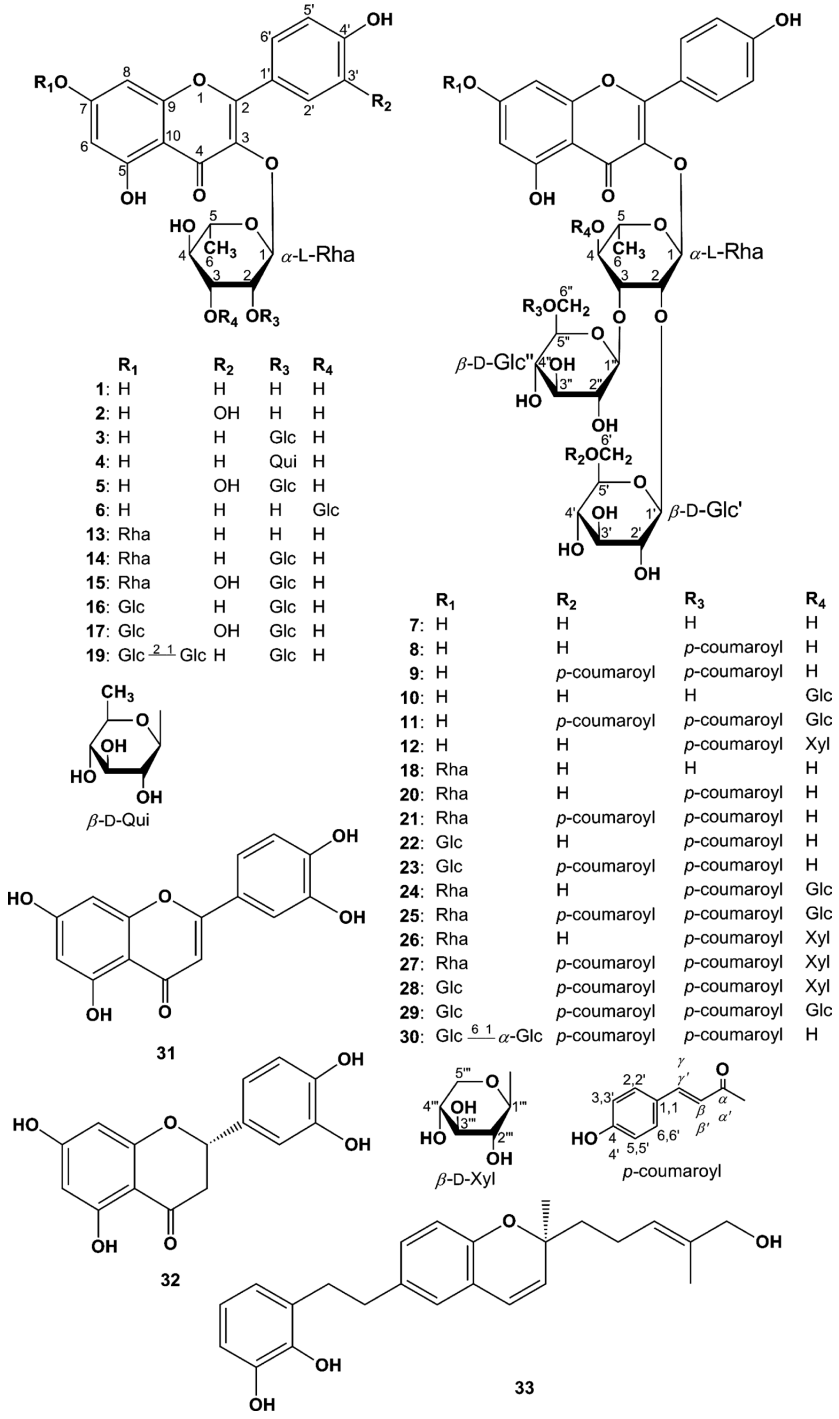
The molecular formula of ternatumoside I (**4**), $C_{27}H_{30}O_{14}$, was established based on a high resolution (HR)-FAB-MS molecular ion at *m/z* 601.1539 ([M+Na]$^+$). The aglycone of **4** was identified as kaempferol, according to observations of 15 carbon signals including twelve aromatic carbons (δ 166.2, 163.3, 161.7, 158.6, 131.9×2, 116.6×2, 122.6, 105.9, 100.0, 94.9), two olefin carbons (δ 159.2, 136.8), and one carbonyl carbon (δ 179.7), and the AX-type aromatic proton [δ 6.38 (1H, d, J=2.0 Hz) and 6.21 (1H, d, J=2.0 Hz)] and AA′XX′-type aromatic proton signals [δ 7.78 (2H, br d, J=9.0 Hz), and 6.95 (2H, br d, J=9.0 Hz)] in the ^{13}C- and ^{1}H-NMR spectroscopic data. Moreover, in the ^{1}H- and ^{13}C-NMR spectra of **4**, two anomeric proton and carbon signals were observed at δ 5.59 (1H, d, J=1.5 Hz), 4.36 (1H, d, J=8.0 Hz) and δ 107.2, 103.2. Thus, **4** was considered to be a kaempferol diglycoside. Acid hydrolysis of **4** afforded L-rhamnose and D-quinovose with kaempferol, and on the basis of ^{1}H-detected heteronuclear multiple quantum coherency (HMQC) and ^{1}H–^{1}H shift correlation spectroscopy (COSY) measurements, the signals at δ 5.59, 103.2 and δ 4.36, 107.2 were assigned at the anomeric proton and carbon of α-L-rhamnopyranose and β-D-quinovopyranose, whose conformations were judged from the ^{1}H-chemical shift or coupling constant of each anomeric proton signal, respectively.[16] In the ^{1}H-detected heteronuclear multiple-bond connectivity (HMBC) measurements, long-range correlations were exhibited between C-3 of the aglycone (δ 136.8) and H-1 of α-L-rhamnopyranose (δ 5.59), and C-2 of α-L-rhamnopyranose (δ 83.0) and H-1′ of β-D-quinovopyranose (δ 4.36). In addition, the rotating frame nuclear Overhauser effect (ROE) difference experiment exhibited a ROE between H-1′ of β-D-quinovopyranose and H-2 of α-L-rhamnopyranose [δ 4.26 (1H, dd, J=3.5, 1.5 Hz)]. Hence, **4** was determined as kaempferol 3-*O*-β-D-quinovopyranosyl-(1→2)-α-L-rhamnopyranoside.

The molecular formula of ternatumoside II (**6**) was suggested to be $C_{27}H_{30}O_{15}$ based on high resolution (HR)-FAB-MS, and **6** was also identified as a kaempferol diglycoside whose component sugars were α-L-rhamnopyranose and β-D-glucopyranose from the NMR spectroscopic data and acid hydrolysis. The sugar linkage of **6** was determined by a ROE difference experiment irradiating the anomeric proton of β-D-glucopyranose and HMBC measurements. A ROE was observed between H-1″ of β-D-glucopyranose [δ 4.49 (1H, d, J=8.0 Hz)] and H-3 of α-L-rhamnopyranose [δ 3.80 (1H, dd, J=9.0, 3.0 Hz)]. The HMBC correlations were shown to be between H-1 of α-L-rhamnopyranose [δ 5.39 (1H, d, J=1.5 Hz)] and C-3 of the aglycone (δ 136.0), H-1″ of β-D-glucopyranose (δ 4.49) and C-3 of α-L-rhamnopyranose (δ 82.7), and H-3 of α-L-rhamnopyranose (δ 3.80) and C-1″ of β-D-glucopyranose (δ 106.0). Thus, **6** was established to be kaempferol 3-*O*-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranoside.

The molecular formulae of ternatumosides III (**8**) and IV (**9**) were identified as $C_{42}H_{46}O_{22}$ and $C_{51}H_{52}O_{24}$, respectively, by HR-FAB-MS. The NMR spectroscopic data for **8** and **9** were similar to those of **7**, and signals due to one and two sets of (*trans*)-*p*-coumaroyl groups were observed in **8** and **9**, respectively. Additionally, both compounds yielded **7** and (*trans*)-*p*-coumaric acid by alkaline hydrolysis. In the homonuclear Haltmann–Hahn (HOHAHA) difference experiment of **8**, irradiation of H-1″ of β-D-glucopyranose [δ 4.54 (1H, d, J=8.0 Hz)] exhibited signal enhancement for H-6″ of β-D-glucopyranose [δ 4.51 (2H, overlapping)]. Moreover, HMBC measurements in **8** revealed long-range correlations between H-6″ of β-D-glucopyranose (δ 4.51) and C-α' of (*trans*)-*p*-coumaroyl group (δ 169.0). Similarly, the

The authors declare no conflict of interest.

* To whom correspondence should be addressed. e-mail: warashin@u-shizuoka-ken.ac.jp



	R_1	R_2	R_3	R_4
1:	H	H	H	H
2:	H	OH	H	H
3:	H	H	Glc	H
4:	H	H	Qui	H
5:	H	OH	Glc	H
6:	H	H	H	Glc
13:	Rha	H	H	H
14:	Rha	H	Glc	H
15:	Rha	OH	Glc	H
16:	Glc	H	Glc	H
17:	Glc	OH	Glc	H
19:	Glc (2→1) Glc	H	Glc	H

	R_1	R_2	R_3	R_4
7:	H	H	H	H
8:	H	H	*p*-coumaroyl	H
9:	H	*p*-coumaroyl	*p*-coumaroyl	H
10:	H	H	H	Glc
11:	H	*p*-coumaroyl	*p*-coumaroyl	Glc
12:	H	H	*p*-coumaroyl	Xyl
18:	Rha	H	H	H
20:	Rha	H	*p*-coumaroyl	H
21:	Rha	*p*-coumaroyl	*p*-coumaroyl	H
22:	Glc	H	*p*-coumaroyl	H
23:	Glc	*p*-coumaroyl	*p*-coumaroyl	H
24:	Rha	H	*p*-coumaroyl	Glc
25:	Rha	*p*-coumaroyl	*p*-coumaroyl	Glc
26:	Rha	H	*p*-coumaroyl	Xyl
27:	Rha	*p*-coumaroyl	*p*-coumaroyl	Xyl
28:	Glc	*p*-coumaroyl	*p*-coumaroyl	Xyl
29:	Glc	*p*-coumaroyl	*p*-coumaroyl	Glc
30:	Glc (6→1) α-Glc	*p*-coumaroyl	*p*-coumaroyl	H

Chart 1. Structure of **1**–**33**

HOHAHA difference experiments of **9** showed signal enhancement for H-6′ and H-6″ of *β*-D-glucopyranose [*δ* 4.50 (1H, overlapping), 4.22 (1H, dd, *J*=12.0, 5.5 Hz) and *δ* 4.52 (1H, dd, *J*=12.0, 2.5 Hz), 4.48 (1H, dd, *J*=12.0, 8.0 Hz)] on irradiating H-1′ and H-1″ of the *β*-D-glucopyranosyl groups [*δ* 4.58 (1H, d, *J*=8.0 Hz) and *δ* 4.57 (1H, d, *J*=8.0 Hz)]. HMBC correlations were observed between H-6′, H-6″ of the *β*-D-glucopyranosyl groups (*δ* 4.22 and *δ* 4.52) and C-*α*, C-*α*′ of the (*trans*)-*p*-coumaroyl groups (*δ* 169.1 and *δ* 169.0) in **9**. Thus, **8** and **9** were established to be kaempferol 3-*O*-[*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-*β*-D-glucopyranosyl-(1→2)-*α*-L-rhamnopyranoside and kaempferol 3-*O*-[*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→2)-*α*-L-rhamnopyranoside, respectively.

Ternatumoside V (**10**) was shown to have the molecular formula $C_{39}H_{50}O_{25}$ by the HR-FAB-MS measurements, and deduced to be a kaempferol tetraglycoside based on the observation of four anomeric carbon and proton signals [*δ* 106.2, 105.4, 104.3, 102.6 and *δ* 4.67 (1H, d, *J*=8.0 Hz), 4.63 (1H, d, *J*=8.0 Hz), 4.56 (1H, d, *J*=8.0 Hz), 5.62 (1H, d, *J*=1.5 Hz)] with signals due to kaempferol in the NMR spectra. Because acid hydrolysis of **10** yielded D-glucose and L-rhamnose with kaempferol, **10** consisted of kaempferol, one

α-L-rhamnopyranosyl group, and three β-D-glucopyranosyl groups. Comparison of the ^{13}C-NMR spectroscopic data of **10** with those of **7** revealed glycosylation shifts around C-4 of L-rhamnopyranose [C-3 (−0.4 ppm), C-4 (+7.3 ppm), C-5 (−0.4 ppm)],[16] suggesting that the β-D-glucopyranosyl group was attached at this position, which was confirmed by a ROE between H-1‴ of β-D-glucopyranose (δ 4.67) and H-4 of α-L-rhamnopyranose [δ 3.75 (1H, t, J=9.0 Hz)]. Thus, **10** was determined as kaempferol 3-*O*-(2,3,4-tri-*O*-β-D-glucopyranosyl)-α-L-rhamnopyranoside.

Ternatumoside VI (**11**) was assigned the molecular formula $C_{57}H_{62}O_{29}$ based on HR-FAB-MS. The NMR spectroscopic data and alkaline hydrolysis suggested that **11** consisted of **10** and two (*trans*)-*p*-coumaroyl groups. As acylation shifts were observed at H-6′ and H-6″ of the β-D-glucopyranosyl groups on comparison of the ^{1}H-NMR spectroscopic data with those of **10**, **11** was determined as kaempferol 3-*O*-[β-D-glucopyranosyl-(1→4)]-[β-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-β-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→2)-α-L-rhamnopyranoside. These esterifications were supported by the observation of long-range correlations between H-6′, H-6″ of the β-D-glucopyranosyl groups [δ 4.47 (1H, dd, J=12.0, 2.5 Hz) and δ 4.50 (2H, overlapping)] and C-α, C-α' of the (*trans*)-*p*-coumaroyl groups (δ 169.1 and δ 169.0) in the HMBC measurements, the same as **9**.

The molecular formula of ternatumoside VII (**12**) was proposed to be $C_{47}H_{54}O_{26}$ based on HR-FAB-MS. Comparison of the NMR spectroscopic data with those of **8** suggested that **12** had one more pentose in its structure. Acid hydrolysis following alkaline hydrolysis yielded L-rhamnose, D-glucose, and D-xylose with kaempferol. On the basis of ^{1}H–^{1}H COSY, HMBC measurements and HOHAHA difference experiments, the assignments of the ^{13}C- and ^{1}H-NMR spectroscopic data were carried out as shown in Tables 1 and 2. In the ROE difference experiment, irradiation of H-1‴ of β-D-xylopyranose [δ 4.64 (1H, d, J=8.0 Hz)] showed a ROE to H-4 of α-L-rhamnopyranose [δ 3.62 (1H, t, J=9.0 Hz)]. The other sugar linkages and the ester function were also confirmed by the ROE difference experiment on irradiation of each anomeric proton and HMBC measurements. Therefore, **12** was established as kaempferol 3-*O*-[β-D-xylopyranosyl-(1→4)]-[β-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→2)-α-L-rhamnopyranoside.

The molecular formulae of ternatumosides VIII (**18**) and IX (**19**) were proposed to be $C_{39}H_{50}O_{24}$ and $C_{39}H_{50}O_{25}$, respectively, based on HR-FAB-MS. The NMR spectroscopic data for **18** and **19** suggested that these compounds were also kaempferol bisdesmosides the same as **13**, **14**, and **16**. The component sugars were identified as two α-L-rhamnopyranosyl groups and two β-D-glucopyranosyl groups for **18**, and one α-L-rhamnopyranosyl group and three β-D-glucopyranosyl groups for **19**, because of assignments of the ^{1}H- and ^{13}C-NMR spectroscopic data on the basis of HOHAHA difference experiments and the second dimensional (2D)-NMR (HMQC, HMBC, and ^{1}H–^{1}H COSY) measurements. The NMR spectroscopic data of **18** showed the sugar sequence attached at the C-3 position of kaempferol to be the same as that in **7**. The remaining α-L-rhamnopyranose was considered to be connected to the C-7 position of kaempferol based on the HMBC correlation from H-1⁗ of this α-L-rhamnopyranose [δ 5.57 (1H, d, J=1.5 Hz)] to C-7 of kaempferol (δ 163.6) and

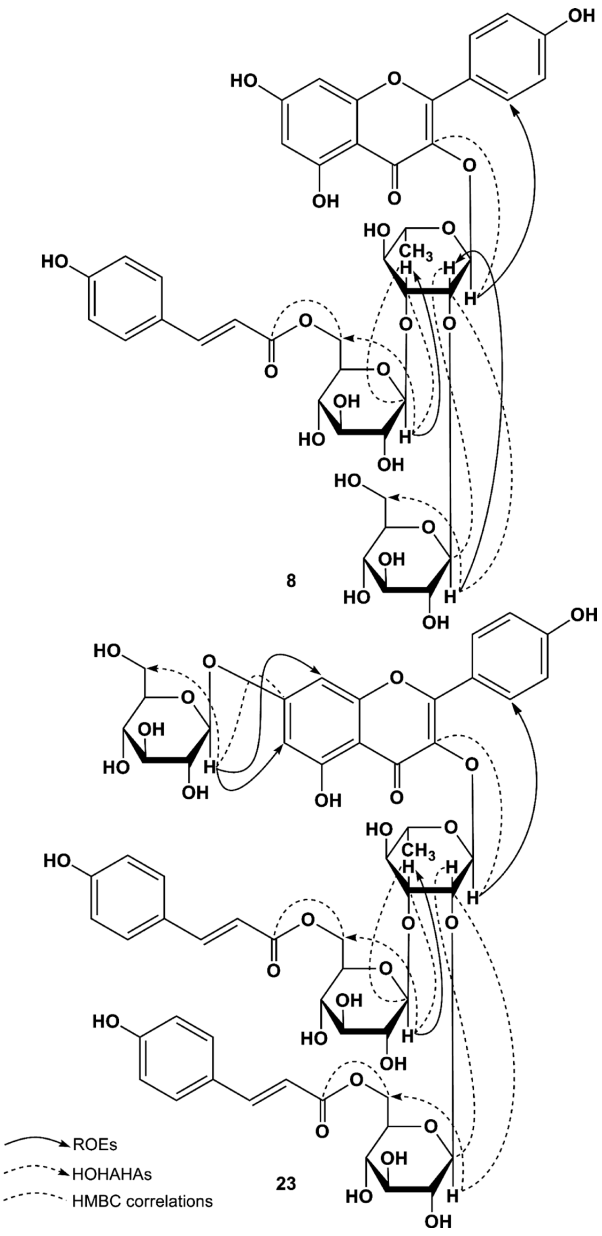


Chart 2. Important ROEs, HOHAHAs, and HMBC Correlations in Ternatumosides III (**8**) and XII (**23**)

ROEs between H-1⁗ of this α-L-rhamnopyranose and H-6 [δ 6.47 (1H, d, J=2.0 Hz)] and H-8 [δ 6.72 (1H, d, J=2.0 Hz)] of kaempferol. Thus, **18** was elucidated as kaempferol 3-*O*-(2,3-di-*O*-β-D-glucopyranosyl)-α-L-rhamnopyranoside-7-*O*-α-L-rhamnopyranoside. The NMR spectroscopic data of **19** showed similarity to those of **16**, but observation of the glycosylation shifts around the C-2⁗ position of the 7-*O*-β-D-glucopyranosyl unit [C-1⁗ (−1.4 ppm), C-2⁗ (+8.8 ppm), C-3⁗ (−0.4 ppm)] indicated that the remaining β-D-glucopyranose was connected to this position. The HMBC correlation between H-1⁗ of β-D-glucopyranose [δ 4.67 (1H, d, J=8.0 Hz)] and C-2⁗ of the 7-*O*-β-D-glucopyranosyl unit (δ 83.6) supported this sugar linkage. Hence, **19** was determined as kaempferol 3-*O*-β-D-glucopyranosyl-(1→2)-α-L-rhamnopyranoside-7-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranoside.

The molecular formulae of ternatumoside X (**20**) and **21** were identified as $C_{48}H_{56}O_{26}$ and $C_{57}H_{62}O_{28}$, respectively,

Table 1. ^{13}C-NMR Spectroscopic Data of Compounds **4**, **6**, **8**–**12**, **18**–**23**, **26**–**29**, and **30**

	4	**6**	**8**	**9**	**10**	**11**	**12**	**18**	**19**	**20**	**21**	**22**	**23**	**26**	**27**	**28**	**29**	**30**
Aglycone moiety																		
C-2	159.2	159.3	158.2[a]	157.6	159.4	157.7	158.2	159.9	159.9	159.0	158.1	158.7	158.1	158.7	158.2	158.2	158.2	158.2
-3	136.8	136.0	135.4	135.9	136.3	136.0	135.5	136.6	136.8	135.6	136.2	135.6	136.1	135.7	136.3	136.3	136.2	136.2
-4	179.7	179.6	179.2	179.2	179.6	179.2	179.1	179.7	179.7	179.3	179.3	179.3	179.3	179.3	179.3	179.3	179.3	179.3
-5	163.3	163.2	163.0	163.1	163.2	163.0	163.0	162.9	162.8	162.7	162.8	162.6	162.7	162.7	162.7	162.6	162.6	162.8
-6	100.0	99.9	99.9	99.8	100.2	99.8	100.0	100.8	101.0	100.7	100.5	100.9	100.8	100.7	100.5	100.8	100.8	100.8
-7	166.2	166.0	165.7	165.5	166.4	165.5	165.9	163.6	164.5	163.5	163.3	164.5	164.2	163.6	163.3	164.2	164.2	164.2
-8	94.9	94.8	94.8	94.8	95.0	94.9	94.9	95.7	96.1	95.4	95.4	96.0	95.8	95.5	95.5	95.9	95.8	95.9
-9	158.6	158.6	158.3[a]	158.1	158.7	158.1	158.2	158.1	158.1	157.8	157.6	157.7	157.6	157.8	157.6	157.5	157.5	157.5
-10	105.9	105.9[a]	105.9[b]	106.1	106.2	106.1	106.0	107.6	107.7	107.6	107.7	107.8	107.9	107.6	107.6	107.9	107.9	108.0
-1′	122.6	122.6	122.6	122.7	122.6	122.7	122.6	122.3	122.4	121.4	122.5	122.4	122.5	122.3	122.4	122.4	122.4	122.5
-2′	131.9	132.0	131.9	131.9	132.0	131.9	131.9	132.1	132.1	132.0	132.0	132.0	132.0	132.0	132.0	132.0	132.0	132.1
-3′	116.6	116.6	116.5[c]	116.5[a]	116.7	116.5[a]	116.6[a]	116.7	116.6	116.6[a]	116.5[a]	116.6[a]	116.5[a]	116.7	116.6[a]	116.5[a]	116.5[a]	116.5
-4′	161.7	161.7	161.6	161.4	161.7	161.4	161.6	161.9	161.8	161.8	161.7	161.8	161.6	161.8	161.7	161.7	161.6	161.6
-5′	116.6	116.6	116.5[c]	116.5[a]	116.7	116.5[a]	116.6[a]	116.7	116.6	116.6[a]	116.5[a]	116.6[a]	116.5[a]	116.7	116.6[a]	116.5[a]	116.5[a]	116.5
-6′	131.9	132.0	131.9	131.9	132.0	131.9	131.9	132.1	132.1	132.0	132.0	132.0	132.0	132.0	132.0	132.0	132.0	132.1
Sugar moieties																		
3-*O*-Sugars																		
	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha	Rha
-1	103.2	103.2	101.5	101.7	102.6	101.7	101.5	102.7	102.6	101.4	101.7	101.4	101.6	101.4	101.7	101.6	101.5[b]	101.8[a]
-2	83.0	71.2[b]	80.6	81.5	80.7	81.6	80.8	80.7	82.6	80.6	81.8[b]	80.7	81.8	80.8	82.0	82.1	81.9	81.8[b]
-3	71.9	82.7	81.9	82.0	81.6	81.2	81.2	82.7	71.8	81.8	81.7[b]	81.8	81.8	81.1	81.0	81.0	81.0	81.7[b]
-4	73.6[a]	72.0	71.7[d]	71.7	78.4	78.3	78.3[b]	71.8[a]	73.5	71.6[b]	71.8	71.6[b]	71.7[b]	78.3[a]	78.4	78.3[b]	78.4[c]	71.8
-5	71.9	71.1[b]	71.7[d]	71.7	70.8	70.7	70.6	71.9[a]	72.0	71.8[b]	71.8[c]	71.8[b]	71.7[b]	70.7	70.6	70.6	70.8	71.8
-6	17.6	17.8	17.7	17.8	18.1	18.0	17.8	17.8	17.6	17.7	17.8	17.7	17.8	17.8	17.8	17.8	18.0	17.8
	Qui		Glc	Glc	Glc	Glc	Glc	Glc	Glc	Glc	Glc	Glc	Glc	Glc	Glc	Glc	Glc	Glc
-1′	107.2	—	106.1[b]	106.1[b]	106.2	106.1	106.0	106.2	107.1	106.0	106.2[d]	106.0	106.2	106.0	106.3	106.3	106.2	106.2
-2′	75.7	—	75.4	75.4[c]	75.5[a]	75.4[b]	75.4	75.5	75.4	75.4	75.4[e]	75.4	75.3[c]	75.4	75.3	75.3[c]	75.3[d]	75.4[c]
-3′	77.7	—	77.9	77.9[d]	77.8[b]	77.9[c]	78.0[c]	78.0[b]	77.9[a]	77.9[c]	77.9	77.9[c]	77.9	78.0[b]	77.9	77.9	77.7[e]	77.9
-4′	76.9	—	71.5[d]	71.9[e]	71.2	71.9	71.4	71.3[c]	71.0[b]	71.5	72.4	71.5[d]	72.3	71.4	72.0	72.0[d]	71.9[f]	71.9[d]
-5′	73.5[a]	—	78.0	75.3[c]	78.0[c]	75.5[b]	78.2[b]	77.8[b]	77.9[a]	78.0[c]	75.5[e]	78.0[c]	75.4	78.2[a]	75.3	75.4[c]	75.4	75.5[c]
-6′	18.0	—	62.9	64.5	62.6	64.5	62.9	62.6	62.4	63.0	64.5	63.0	64.5	62.9	64.5	64.5	64.5	64.5
		Glc	Glc	Glc	Glc	Glc	Glc	Glc		Glc	Glc	Glc	Glc	Glc	Glc	Glc	Glc	Glc
-1″	—	106.0[a]	106.2[b]	106.3[b]	105.4	105.5	105.5	105.9	—	106.3	106.3[d]	106.3	106.3	105.5	105.5	105.4	105.5	106.2
-2″	—	75.4	75.4	75.5[c]	75.4[a]	75.3[b]	75.4	75.5	—	75.4	75.4[e]	75.4	75.5[c]	75.4	75.5	75.5[c]	75.5[d]	75.3[c]
-3″	—	77.8	77.9	77.8[d]	77.7[b]	78.4	77.9[c]	77.9[b]	—	77.9[c]	77.9	77.9[c]	77.9	77.9[b]	78.2	78.2	78.3	77.9
-4″	—	71.8	72.4	72.3[e]	71.2	72.5	72.6	71.2[c]	—	72.5	72.0[c]	72.5	72.0[b]	72.7	72.5	72.5[d]	72.5[f]	72.3[d]
-5″	—	77.8	76.0	76.0	77.9[c]	76.1	76.1	77.7	—	76.0	76.1	76.0	76.0	76.1	76.1	76.1	76.1	76.0
-6″	—	62.3	65.2	65.2	62.4	65.3	65.3	62.3	—	65.3	65.3	65.3	65.3	65.3	65.3	65.3	65.3	65.3

					Glc	Glc	Xyl							Xyl	Xyl	Xyl	Glc	
-1‴	—	—	—	—	104.3	104.1	104.8	—	—	—	—	—	—	104.7	104.3	104.8	104.1	—
-2‴	—	—	—	—	75.7	75.9	75.8	—	—	—	—	—	—	75.8	75.8	75.8	75.9	—
-3‴	—	—	—	—	78.6	78.7	78.8	—	—	—	—	—	—	78.8	78.7	78.7	78.7	—
-4‴	—	—	—	—	71.8	71.9	71.4	—	—	—	—	—	—	71.4	71.5	71.4[e]	72.0[f]	—
-5‴	—	—	—	—	78.1[c]	77.7[c]	66.9	—	—	—	—	—	—	66.9	67.0	67.0	77.8[e]	—
-6‴	—	—	—	—	63.0	63.0	—	—	—	—	—	—	—	—	—	—	63.0	—
7-*O*-Sugar																		
								Rha	Glc	Rha	Rha	Glc	Glc	Rha	Rha	Glc	Glc	Glc
-1⁗	—	—	—	—	—	—	—	99.9	100.3	100.0	100.0	101.6	101.7	100.0	100.0	101.6	101.6[b]	101.7[a]
-2⁗	—	—	—	—	—	—	—	71.7[a]	83.6	71.8[a]	71.8	74.8	74.8	71.8	71.8	74.9	74.8	74.8
-3⁗	—	—	—	—	—	—	—	72.1	77.5	72.2	72.2	77.9[c]	77.9	72.2	72.2	77.9	77.9[e]	77.9
-4⁗	—	—	—	—	—	—	—	73.6	71.2[b]	73.7	73.8	71.4[d]	71.3	73.7	73.8	71.5[e]	71.4	71.2
-5⁗	—	—	—	—	—	—	—	71.1[c]	77.8[a]	71.2	71.2	78.4	78.3	71.2	71.2	78.4[b]	78.3[c]	76.7
-6⁗	—	—	—	—	—	—	—	18.1	62.2	18.1	18.2	62.6	62.5	18.1	18.2	62.6	62.5	67.6
									Glc									*α*-Glc
-1⁗′	—	—	—	—	—	—	—	—	105.5	—	—	—	—	—	—	—	—	100.1
-2⁗′	—	—	—	—	—	—	—	—	76.0	—	—	—	—	—	—	—	—	73.8[e]
-3⁗′	—	—	—	—	—	—	—	—	78.1[a]	—	—	—	—	—	—	—	—	75.3
-4⁗′	—	—	—	—	—	—	—	—	71.0[b]	—	—	—	—	—	—	—	—	71.8
-5⁗′	—	—	—	—	—	—	—	—	78.0[a]	—	—	—	—	—	—	—	—	73.7[e]
-6⁗′	—	—	—	—	—	—	—	—	62.4	—	—	—	—	—	—	—	—	62.6
Ester moieties																		
(R_2)-*α*	—	—	—	169.1[f]	—	169.1[d]	—	—	—	—	169.0	—	169.0[d]	—	169.0	169.0[f]	169.0[g]	169.0
-*β*	—	—	—	115.0[g]	—	115.1[e]	—	—	—	—	115.0[f]	—	115.1[e]	—	115.0[b]	115.0[g]	115.1[h]	115.1[f]
-*γ*	—	—	—	146.6	—	146.6	—	—	—	—	146.5	—	146.5	—	146.6[c]	146.6[h]	146.6[i]	146.6[g]
-1	—	—	—	127.2	—	127.2	—	—	—	—	127.1	—	127.1	—	127.1	127.1	127.1	127.2
-2	—	—	—	131.1	—	131.1	—	—	—	—	131.0	—	131.0	—	131.1	131.0	131.0	131.0
-3	—	—	—	116.7	—	116.7	—	—	—	—	116.7	—	116.7	—	116.7	116.7	116.7	116.7
-4	—	—	—	161.0	—	161.0	—	—	—	—	161.1	—	160.9	—	161.1	161.0	160.9	161.1
-5	—	—	—	116.7	—	116.7	—	—	—	—	116.7	—	116.7	—	116.7	116.7	116.7	116.7
-6	—	—	—	131.1	—	131.1	—	—	—	—	131.0	—	131.0	—	131.1	131.0	131.0	131.0
(R_3)-*α*′	—	—	169.0	169.0[f]	—	169.0[d]	169.0	—	—	168.9	169.0	168.9	168.9[d]	168.9	169.0	168.9[f]	168.9[g]	169.0
-*β*′	—	—	114.9	114.9[g]	—	114.9[e]	114.9	—	—	115.0	114.9[f]	115.0	115.0[e]	115.0	114.9[b]	115.1[g]	115.0[h]	115.0[f]
-*γ*′	—	—	146.9	147.0	—	146.9	146.8	—	—	146.8	146.9	146.8	146.8	146.6	146.7[c]	146.7[h]	146.7[i]	146.8[g]
-1′	—	—	126.8	126.8	—	126.7	126.7	—	—	126.7	126.7	126.8	126.8	126.7	126.6	126.7	126.7	126.8
-2′	—	—	130.7	130.8	—	130.7	130.6	—	—	130.6	130.6	130.6	130.6	130.4	130.5	130.5	130.5	130.7
-3′	—	—	116.4[c]	116.4[a]	—	116.4[a]	116.4[a]	—	—	116.4[a]	116.4[a]	116.4[a]	116.5[a]	116.4	116.4[a]	116.4[a]	116.4[a]	116.5
-4′	—	—	160.9	160.9	—	160.9	160.9	—	—	160.8	160.8	160.7	160.6	160.8	160.8	160.6	160.6	160.7
-5′	—	—	116.4[c]	116.4[a]	—	116.4[a]	116.4[a]	—	—	116.4[a]	116.4[a]	116.4[a]	116.5[a]	116.4	116.4[a]	116.4[a]	116.4[a]	116.5
-6′	—	—	130.7	130.8	—	130.7	130.6	—	—	130.6	130.6	130.6	130.6	130.4	130.5	130.5	130.5	130.7

Measured in MeOH-d_4 solution at 35°C. [a–i]Interchangeable in each column. Data of the ester moieties may be interchangeable in each column. Rha: *α*-L-rhamnopyranose, Qui: *β*-D-quinovopyranose, Glc: *β*-D-glucopyranose, *α*-Glc: *α*-D-glucopyranose Xyl: *β*-D-xylopyranose.

based on HR-FAB-MS. Alkaline hydrolysis of these compounds afforded **18** and (*trans*)-*p*-coumaric acid. Similarly, the NMR spectra exhibited signals due to one set and two sets of (*trans*)-*p*-coumaroyl groups in **20** and **21**, respectively, together with those of **18**. The NMR spectroscopic data of the 3-*O*-linked sugar and ester moieties in **20** and **21** resemble those of **8** and **9**. **20** showed a long-range correlation between H-6″ of *β*-D-glucopyranose [*δ* 4.45 (1H, dd, *J*=12.0, 2.0 Hz)] and C-*α*′ of the (*trans*)-*p*-coumaroyl group (*δ* 168.9), and **21** showed correlations between H-6′, H-6″ of the *β*-D-glucopyranosyl groups [*δ* 4.20 (1H, dd, *J*=12.0, 6.0 Hz) and *δ* 4.48 (1H, dd, *J*=12.0, 2.5 Hz)] and C-*α*, C-*α*′ of the (*trans*)-*p*-coumaroyl groups (*δ* 169.0×2) in the HMBC measurements. Thus, **20** and **21** were established as kaempferol 3-*O*-[*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-*β*-D-glucopyranosyl-(1→2)-*α*-L-rhamnopyranoside-7-*O*-*α*-L-rhamnopyranoside and kaempferol 3-*O*-[*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→2)-*α*-L-rhamnopyranoside-7-*O*-*α*-L-rhamnopyranoside, respectively. **21** has been reported previously, but only LC-MS data were described. Accordingly, other physical data including NMR spectroscopic data are mentioned in this report.

Ternatumosides XI (**22**) and XII (**23**) were proposed to have the molecular formulae $C_{48}H_{56}O_{27}$ and $C_{57}H_{62}O_{29}$, based on HR-FAB-MS, and were larger than **20** and **21** by an oxygen atom, respectively. The NMR spectroscopic data for the aglycone and 3-*O*-linked sugar and ester moieties of **22** and **23** were consistent with those of **20** and **21**. In both compounds, each sugar unit connected to C-7 of the aglycone was determined to be *β*-D-glucopyranose, corresponding to the NMR spectroscopic data of **16**. So, **22** and **23** were identified as kaempferol 3-*O*-[*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-*β*-D-glucopyranosyl-(1→2)-*α*-L-rhamnopyranoside-7-*O*-*β*-D-glucopyranoside and kaempferol 3-*O*-[*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→2)-*α*-L-rhamnopyranoside-7-*O*-*β*-D-glucopyranoside, respectively. These structures were supported by the HMBC measurements, ROE, and HOHAHA difference experiments irradiating the anomeric protons (see Chart 2).

HR-FAB-MS revealed the molecular formulae of ternatumoside**s** XIII (**26**) and XIV (**27**) to be $C_{53}H_{64}O_{30}$ and $C_{62}H_{70}O_{32}$, respectively. The ^{13}C- and ^{1}H-NMR spectroscopic data of **26** and **27** were similar to those of **24** and **25**, but the characteristic C-5 and H-5 signals of *β*-D-xylopyranose were observed at *δ* 66.9, *δ* 3.76 (1H, dd, *J*=11.5, 5.5 Hz), 3.13 (1H, t, *J*=11.5 Hz) in **26** and *δ* 67.0, *δ* 3.78 (1H, dd, *J*=11.5, 5.5 Hz), 3.15 (1H, t, *J*=11.5 Hz) in **27** the same as in **12**. Assignments of the ^{13}C- and ^{1}H-NMR spectroscopic data (Tables 1 and 2) were made on the basis of 2D-NMR measurements and HOHAHA difference experiments. The above *β*-D-xylopyranosyl unit was connected to the C-4 position of *α*-L-rhamnopyranose, which was supported by the ROE difference experiment on irradiation of H-1‴ of *β*-D-xylopyranose [**26**: *δ* 4.65 (1H, d, *J*=8.0 Hz); **27**: *δ* 4.68 (1H, d, *J*=8.0 Hz)] and HMBC measurements. Hence, **26** and **27** were identified as kaempferol 3-*O*-[*β*-D-xylopyranosyl-(1→4)]-[*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-*β*-D-glucopyranosyl-(1→2)-*α*-L-rhamnopyranoside-7-*O*-*α*-L-rhamnopyranoside and kaempferol 3-*O*-[*β*-D-xylopyranosyl-(1→4)]-[*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→2)-*α*-L-rhamnopyranoside-7-*O*-*α*-L-rhamnopyranoside, respectively.

The molecular formulae of ternatumosides XV (**28**) and XVI (**29**) were established as $C_{62}H_{70}O_{33}$ and $C_{63}H_{72}O_{34}$, respectively. Comparing the NMR spectroscopic data of **28** with those of **23** and **27**, **28** was presumed to have a *β*-D-glucopyranosyl group instead of *α*-L-rhamnopyranosyl group at the C-7 position of aglycone in **27**. It was assumed that the *β*-D-glucopyranosyl group in **29** was replaced with a *β*-D-xylopyranosyl group at the C-4 position of *α*-L-rhamnopyranose in **28** on comparison of the NMR spectroscopic data with those of **25** and **28**. These structures were confirmed based on the ROE and HOHAHA difference experiments and the 2D-NMR measurements. **28** and **29** were established as kaempferol 3-*O*-[*β*-D-xylopyranosyl-(1→4)]-[*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→2)-*α*-L-rhamnopyranoside-7-*O*-*β*-D-glucopyranoside and kaempferol 3-*O*-[*β*-D-glucopyranosyl-(1→4)]-[*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→2)-*α*-L-rhamnopyranoside-7-*O*-*β*-D-glucopyranoside, respectively.

Ternatumoside XVII (**30**) was found to have the molecular formula, $C_{63}H_{72}O_{34}$, based on HR-FAB-MS. The NMR spectroscopic data suggested that **30** contained kaempferol, two *p*-coumaroyl groups, and five sugars. Because acid hydrolysis following alkaline hydrolysis of **30** yielded L-rhamnose and D-glucose and the ^{13}C-NMR spectrum showed one signal due to C-6 of L-rhamnopyranose at *δ* 17.8, these sugars consisted of one *α*-L-rhamnopyranose and four D-glucopyranoses. In the ^{1}H-NMR spectrum, three anomeric proton signals due to *β*-D-glucopyranoses were observed at *δ* 5.05 (1H, d-like, *J*=8.0 Hz), 4.58 (1H, d, *J*=8.0 Hz), and 4.57 (1H, d, *J*=8.0 Hz) with that of *α*-L-rhamnopyranose at *δ* 5.81 (1H, br s), which were similar to those of **23**. The *J* value of the anomeric proton signal due to the remaining D-glucopyranosyl unit at *δ* 4.90 (1H, d, *J*=4.0 Hz) verified that this D-glucopyranose has an *α*-form. The similarity of the NMR spectroscopic data of **30** to those of **23** indicated that **30** contained **23**. In the ROE difference experiment, irradiation of the above anomeric proton due to *α*-D-glucopyranose exhibited a ROE to H-6⁗ of the 7-*O*-*β*-D-glucopyranosyl unit [*δ* 3.86 (1H, dd, *J*=11.5, 2.0 Hz)]. Thus, **30** was determined as kaempferol 3-*O*-[*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→3)]-*β*-D-6-*O*-[4-hydroxy-(*E*)-cinnamoyl]-glucopyranosyl-(1→2)-*α*-L-rhamnopyranoside-7-*O*-*α*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranoside. The ^{13}C- and ^{1}H-NMR spectroscopic data of the 7-*O*-sugar chain were consistent with those of rhodioloside B[17] and genipin 1-*O*-isomaltoside.[18] This structure was supported by the HMBC measurements and ROE difference experiments irradiating other anomeric protons.

Some *p*-coumarated flavonoid glycosides were afforded in this investigation of the constituents from *B. ternatum*. Because these compounds are found in various families including Apocynaceae, Lamiaceae, Lecythidaceae, Leguminosae, Liliaceae, Primulaceae, Ranunculaceae, Resedaceae, Sapindaceae, and Teaceae, they are not considered to be characteristic constituents in the Ophiolossaceaus family. However, to the best of our knowledge, this is the first report about *p*-coumarated flavonoid glycosides from this family.

Previous reports described that *Botrychium virginianum* (*Japanobotrychium virginianum*) which belongs to the Ophiolossaceaus family caused the proliferation of normal human skin fibroblasts and inhibition of melanin synthesis.[1] *B. ternatum* also belongs to the Ophiolossaceaus family. So, we examined whether the MeOH extract, the MeOH–H_2O (9 : 1) layer from the Et_2O-soluble fraction, the MeOH–H_2O (7 : 3) eluate from the porous polymer gel, and the flavonoid glycosides **2**, **3**, **5**, **7**, **8**, **14**, **18**, **21**, **23**, and **25** from *B. ternatum* cause the proliferation of normal human skin fibroblasts. The compounds and the MeOH–H_2O (7 : 3) eluate had no effect on the proliferation of fibroblasts at 100–10 μg/mL. The MeOH extract and the MeOH–H_2O (9 : 1) layer showed cytotoxicity against fibroblasts at 100 – 1.0 μg/mL. Secondly, in the assay of the cosmetic field, we examined the tyrosinase inhibition of the MeOH extract, the MeOH–H_2O (1 : 1 and 7 : 3) eluates from the porous polymer gel, and the flavonoid glycosides **5**, **7**, **22**, **23**, **25**, **27**, and **29** from *B. ternatum* at 400 μg/mL. But, they did not show inhibitory activity against tyrosinase. The compounds and fractions derived from *B. ternatum* showed no effects in our assays of the cosmetic field. Thus, we are interested in the difference of the constituents in *B. ternatum* and *B. virginianum* from the viewpoints of the biological activities and chemotaxonomy. Because *p*-coumarated flavonoid glycosides from *Aconitum anthora* are reported to have the antioxidant activity,[19] the compounds derived from *B. ternatum* may also reveal this activity.

Experimental

General Procedures The instrumental analysis was described previously.[20]

Plant Materials The whole *B. ternatum* plants were purchased from Anguo City Ruikang Herb Co., Ltd. in China in 2010. The dried materials were stored in a herbarium of the University of Shizuoka (voucher number, M-4396).

Extraction and Isolation The dried whole plants of *B. ternatum* (2.7 kg) were extracted twice with MeOH under reflux for 3 h. The extract was concentrated under reduced pressure and the residue was suspended in water (2 L). This suspension was successively extracted with Et_2O (2 L). The Et_2O extract was evaporated dry, and the resulting residue was partitioned between the *n*-hexane-soluble fraction and MeOH–H_2O (9 : 1)-soluble fraction. The MeOH–H_2O (9 : 1) fraction was concentrated, and the residue was subjected to silica gel column chromatography with a $CHCl_3$–MeOH (98 : 2→85 : 15, v/v) system to obtain seven fractions. (A (1.70 g), B (397 mg), C (1.16 g), D (199 mg), E (1.59 g), F (602 mg), and G (739 mg)). Using semi-preparative HPLC (Capcellpak ODS-UG80 30 mm i.d.×25 cm, YMC-ODS 20 mm i.d.×25 cm (MeCN–H_2O (25 : 75, and 1 : 1, v/v), and MeOH–H_2O (1 : 1, and 75 : 25, v/v) and recrystallization (MeOH), fraction B (397 mg) afforded **33** (19 mg). Fraction D (199 mg) yielded **31** (4 mg) and **32** (5 mg).

The H_2O layer of the MeOH extract was passed through a porous polymer gel (Mitsubishi Chemical Co., Diaion HP-20) column with absorbed material being eluted with MeOH–H_2O 1 : 1 (5 L), 7 : 3 (5 L), and MeOH (5 L). The MeOH–H_2O 1 : 1 and 7 : 3 fractions were dried *in vacuo*, respectively (8.5 g and 4.2 g). The residue of the 7 : 3 fraction (2.0 g) was subjected to semi-preparative HPLC (Develosil-ODS-15/30 50 mm i.d.×100 cm (MeCN–H_2O 2 : 8→25 : 75, v/v), Capcellpak ODS-UG80 30 mm i.d.×25 cm, YMC-ODS 20 mm i.d.×25 cm (MeCN–H_2O (17.5 : 82.5 and 2 : 8, v/v), MeOH–H_2O (4 : 6, 45 : 55, and 1 : 1, v/v)). This residue yielded **1** (8 mg), **2** (13 mg), **3** (50 mg), **4** (4 mg), **5** (51 mg), **6** (6 mg), **7** (49 mg), **8** (14 mg), **9** (10 mg), **11** (3 mg), **12** (5 mg), **13** (3 mg), **14** (21 mg), **21** (12 mg), **23** (131 mg), **25** (30 mg), and **27** (29 mg). The residue of the MeOH–H_2O (1 : 1) fraction (8.5 g) was subjected to silica gel column chromatography with the $CHCl_3$–MeOH–H_2O (90 : 10 : 1→75 : 25 : 1, v/v) system to obtain nine fractions (A (606 mg), B (595 mg), C (131 mg) D (745 mg), E (350 mg), F (885 mg), G (667 mg), H (1.88 g), and I (1.57 g)). Using semi-preparative HPLC (Inertsil ODS-3 30 mm i.d.×50 cm, Capcellpak ODS-UG80 30 mm i.d.×25 cm, YMC-ODS 20 mm i.d.×25 cm (MeCN–H_2O (15 : 85, 17.5 : 82.5, 2 : 8, and 22.5 : 77.5, v/v), and MeOH–H_2O (4 : 6, and 45 : 55, v/v)), fraction D (86 mg) afforded **3** (55 mg) and **5** (4 mg). Fraction F (112 mg) yielded **5** (35 mg). Fraction G (333 mg) gave **5** (3 mg), **7** (54 mg), and **14** (30 mg). Fraction H (300 mg) produced **15** (3 mg), **16** (6 mg), **18** (25 mg), **20** (6 mg), and **23** (55 mg). Fraction I (942 mg) provided **10** (9 mg), **17** (6 mg), **18** (10 mg), **19** (53 mg), **22** (23 mg), **24** (10 mg), **26** (16 mg), **28** (12 mg), **29** (17 mg), and **30** (8 mg).

Ternatumoside I (**4**): Yellow amorphous powder. $[\alpha]_D^{20}$ −119 (c=0.39, MeOH). FAB-MS m/z: 601 $[M+Na]^+$. HR-FAB-MS m/z: 601.1539 (Calcd for $C_{27}H_{30}O_{14}Na$: 601.1533). UV λ_{max} (MeOH) nm (log ε): 266 (4.26), 340 (4.10).

Ternatumoside II (**6**): Yellow amorphous powder. $[\alpha]_D^{19}$ −110 (c=0.54, MeOH). FAB-MS m/z: 617 $[M+Na]^+$, 595 $[M+H]^+$. HR-FAB-MS m/z: 617.1511, 595.1675 (Calcd for $C_{27}H_{30}O_{15}Na$: 617.1482 and $C_{27}H_{31}O_{15}$: 595.1663). UV λ_{max} (MeOH) nm (log ε): 266 (4.25), 344 (4.08).

Ternatumoside III (**8**): Yellow amorphous powder. $[\alpha]_D^{19}$ +11 (c=0.68, MeOH). FAB-MS m/z: 925 $[M+Na]^+$, 903 $[M+H]^+$. HR-FAB-MS m/z: 925.2371, 903.2583 (Calcd for $C_{42}H_{46}O_{22}Na$: 925.2378 and $C_{42}H_{47}O_{22}$: 903.2559). UV λ_{max} (MeOH) nm (log ε): 268 (4.38), 315 (4.45).

Ternatumoside IV (**9**): Yellow amorphous powder. $[\alpha]_D^{20}$ −7.7 (c=0.97, MeOH). FAB-MS m/z: 1071 $[M+Na]^+$. HR-FAB-MS m/z: 1071.2783 (Calcd for $C_{51}H_{52}O_{24}Na$: 1071.2745). UV λ_{max} (MeOH) nm (log ε): 223 (sh), 270 (4.47), 303 (sh), 314 (4.68).

Ternatumoside V (**10**): Yellow amorphous powder. $[\alpha]_D^{26}$ −89 (c=0.91, MeOH). FAB-MS m/z: 941 $[M+Na]^+$. HR-FAB-MS m/z: 941.2563 (Calcd for $C_{39}H_{50}O_{25}Na$: 941.2539). UV λ_{max} (MeOH) nm (log ε): 266 (4.28), 345 (4.09).

Ternatumoside VI (**11**): Yellow amorphous powder. $[\alpha]_D^{20}$ −20 (c=0.32, MeOH). FAB-MS m/z: 1233 $[M+Na]^+$. HR-FAB-MS m/z: 1233.3270 (Calcd for $C_{57}H_{62}O_{29}Na$: 1233.3274). UV λ_{max} (MeOH) nm (log ε): 222 (sh), 270 (4.51), 305 (sh), 314 (4.69).

Ternatumoside VII (**12**): Yellow amorphous powder. $[\alpha]_D^{19}$ −21 (c=0.47, MeOH). FAB-MS m/z: 1057 $[M+Na]^+$. HR-FAB-MS m/z: 1057.2799 (Calcd for $C_{47}H_{54}O_{26}Na$: 1057.2800). UV λ_{max} (MeOH) nm (log ε): 268 (4.42), 315 (4.47).

Ternatumoside VIII (**18**): Yellow amorphous powder. $[\alpha]_D^{18}$ −146 (c=1.00, MeOH). FAB-MS m/z: 925 $[M+Na]^+$, 903 $[M+H]^+$. HR-FAB-MS m/z: 925.2612 (Calcd for $C_{39}H_{50}O_{24}Na$: 925.2590). UV λ_{max} (MeOH) nm (log ε): 266 (4.32), 322 (sh), 345 (4.17).

Ternatumoside IX (**19**): Yellow amorphous powder. $[\alpha]_D^{24}$ −134 (c=0.84, MeOH). FAB-MS m/z: 941 $[M+Na]^+$, 919 $[M+H]^+$. HR-FAB-MS m/z: 941.2541, 919.2714 (Calcd for $C_{39}H_{50}O_{25}Na$: 941.2539 and $C_{39}H_{51}O_{25}$: 919.2719). UV λ_{max}

Table 2. ^{1}H-NMR Spectroscopic Data of Compounds **4**, **6**, **8**–**12**, **18**–**23**, **26**–**29**, and **30**

	4	**6**	**8**	**9**	**10**
Aglycone moiety					
H-6	6.21 (d, 2.0)	6.22 (d, 2.0)	6.17 (d, 2.0)	6.12 (d, 2.0)	6.22 (d, 2.0)
-8	6.38 (d, 2.0)	6.39 (d, 2.0)	6.24 (d, 2.0)	6.11 (d, 2.0)	6.39 (d, 2.0)
-2′,6′	7.78 (brd, 9.0)	7.79 (brd, 9.0)	7.75 (brd, 9.0)	7.68 (brd, 9.0)	7.79 (brd, 9.0)
-3′,5′	6.95 (brd, 9.0)	6.95 (brd, 9.0)	6.94 (brd, 9.0)	6.91 (brd, 9.0)	6.96 (brd, 9.0)
3-*O*-Sugars					
	Rha	Rha	Rha	Rha	Rha
H-1	5.59 (d, 1.5)	5.39 (d, 1.5)	5.82 (d, 1.5)	5.81 (d, 1.5)	5.62 (d, 1.5)
-2	4.26 (dd, 3.5, 1.5)	4.42 (dd, 3.0, 1.5)	4.51*	4.57*	4.57 (dd, 3.5, 1.5)
-3	3.80 (dd, 9.5, 3.5)	3.80 (dd, 9.0, 3.0)	3.82 (dd, 9.5, 3.0)	3.88 (dd, 9.5, 3.5)	4.15 (dd, 9.0, 3.5)
-4	3.23*	3.51 (t, 9.0)	3.49 (t, 9.5)	3.52 (t, 9.5)	3.75 (t, 9.0)
-5	3.54 (dq, 9.5, 6.0)	3.47*	3.32 (m)	3.41*	3.53 (dq, 9.0, 6.0)
-6	0.97 (d, 6.0)	0.99 (d, 6.0)	0.93 (d, 6.0)	1.00 (d, 6.0)	1.04 (d, 6.0)
	Qui		Glc	Glc	Glc
H-1′	4.36 (d, 8.0)	—	4.57 (d, 8.0)	4.58 (d, 8.0)	4.56 (d, 8.0)
-2′	3.22 (dd, 9.0, 8.0)	—	3.21 (dd, 9.0, 8.0)	3.26 (dd, 9.0, 8.0)	3.22 (dd, 9.0, 8.0)
-3′	3.30*	—	3.39 (t, 9.0)	3.42 (t, 9.0)	3.38 (t, 9.0)
-4′	2.95 (t, 9.0)	—	3.32*	3.33 (t, 9.0)	3.32*
-5′	3.25 (dq, 9.0, 6.0)	—	3.32*	3.52*	3.22*
-6′	1.17 (d, 6.0)	—	3.81 (dd, 12.0, 2.0)	4.50*	3.71 (dd, 12.0, 2.0)
	—		3.69 (dd, 12.0, 5.0)	4.22 (dd, 12.0, 5.5)	3.66 (dd, 12.0, 5.0)
		Glc	Glc	Glc	Glc
H-1″	—	4.49 (d, 8.0)	4.54 (d, 8.0)	4.57 (d, 8.0)	4.63 (d, 8.0)
-2″	—	3.31*	3.35 (dd, 9.0, 8.0)	3.36 (dd, 9.0, 8.0)	3.29*
-3″	—	3.41 (m)	3.46 (t, 9.0)	3.46 (t, 9.0)	3.40*
-4″	—	3.35*	3.30 (t, 9.0)	3.31*	3.40*
-5″	—	3.35*	3.71 (m)	3.70 (m)	3.40*
-6″	—	3.86 (dd, 12.0, 2.0)	4.51 (2H, *)	4.52 (dd, 12.0, 2.5)	3.92 (brd, 12.0)
	—	3.76 (dd, 12.0, 4.5)	—	4.48 (dd, 12.0, 8.0)	3.79 (brd, 12.0)
					Glc
H-1‴	—	—	—	—	4.67 (d, 8.0)
-2‴	—	—	—	—	3.12 (t, 8.0)
-3‴	—	—	—	—	3.31*
-4‴	—	—	—	—	3.27*
-5‴	—	—	—	—	3.25*
	—	—	—	—	—
-6‴	—	—	—	—	3.82 (dd, 12.0, 2.0)
	—	—	—	—	3.64 (dd, 12.0, 5.0)
7-*O*-Sugar					
H-1⁗	—	—	—	—	—
-2⁗	—	—	—	—	—
-3⁗	—	—	—	—	—
-4⁗	—	—	—	—	—
-5⁗	—	—	—	—	—
-6⁗	—	—	—	—	—
	—	—	—	—	—
H-1⁗′	—	—	—	—	—
-2⁗′	—	—	—	—	—
-3⁗′	—	—	—	—	—
-4⁗′	—	—	—	—	—
-5⁗′	—	—	—	—	—
-6⁗′	—	—	—	—	—
	—	—	—	—	—
Ester moieties					
(R_2) H-β	—	—	—	6.12 (d, 16.0)	—
-γ	—	—	—	7.48 (d, 16.0)	—
-2,6	—	—	—	7.26 (brd, 8.5)	—
-3,5	—	—	—	6.69 (brd, 8.5)	—
(R_3) H-β′	—	—	6.26 (d, 16.0)	6.24 (d, 16.0)	—
-γ′	—	—	7.56 (d, 16.0)	7.54 (d, 16.0)	—
-2′,6′	—	—	7.12 (brd, 8.5)	7.11 (brd, 8.5)	—
-3′,5′	—	—	6.40 (brd, 8.5)	6.42 (brd, 8.5)	—

Table 2. (Continued)

	11	12	18	19	20
Aglycone moiety					
H-6	6.08 (d, 2.0)	6.16 (d, 2.0)	6.47 (d, 2.0)	6.50 (d, 2.0)	6.39 (d, 2.0)
-8	6.11 (d, 2.0)	6.21 (d, 2.0)	6.72 (d, 2.0)	6.74 (d, 2.0)	6.56 (d, 2.0)
-2′,6′	7.66 (brd, 8.5)	7.72 (brd, 8.5)	7.81 (brd, 9.0)	7.80 (brd, 9.0)	7.79 (brd, 8.5)
-3′,5′	6.90 (brd, 8.5)	6.93 (brd, 8.5)	6.97 (brd, 9.0)	6.94 (brd, 9.0)	6.96 (brd, 8.5)
3-*O*-Sugars					
	Rha	Rha	Rha	Rha	Rha
H-1	5.69 (d, 1.5)	5.71 (d, 1.5)	5.67 (d, 1.5)	5.73 (d, 1.5)	5.85 (d, 1.5)
-2	4.52 (dd, 3.5, 1.5)	4.46 (dd, 3.5, 1.5)	4.55*	4.31 (dd, 3.5, 1.5)	4.50 (dd, 3.5, 1.5)
-3	4.12 (dd, 9.5, 3.5)	4.06 (dd, 9.0, 3.5)	3.93*	3.81 (dd, 9.5, 3.5)	3.82 (dd, 9.5, 3.5)
-4	3.75 (t, 9.5)	3.62 (t, 9.0)	3.54*	3.33 (t, 9.5)	3.49 (t, 9.5)
-5	3.47*	3.25 *	3.54*	3.41*	3.23*
-6	1.04 (d, 6.0)	0.90 (d, 6.5)	1.00 (d, 6.0)	0.95 (d, 6.0)	0.93 (d, 6.0)
	Glc	Glc	Glc	Glc	Glc
H-1′	4.57 (d, 8.0)	4.55 (d, 8.0)	4.55 (d, 8.0)	4.44 (d, 8.0)	4.57 (d, 8.0)
-2′	3.26 (t, 8.0)	3.21 (dd, 9.0, 8.0)	3.21 (dd, 9.0, 8.0)	3.24 (dd, 9.0, 8.0)	3.21 (dd, 9.0, 8.0)
-3′	3.41 (t, 8.0)	3.40 (t, 9.0)	3.39 (t, 9.0)	3.36 (t, 9.0)	3.39 (t, 9.0)
-4′	3.31*	3.36*	3.32*		3.32*
-5′	3.48*	3.32*	3.23 (m)	3.24*	3.32*
-6′	4.47 (dd, 12.0, 2.5)	3.78 (dd, 12.0, 2.0)	3.71 (dd, 12.0, 2.5)	3.73*	3.84*
	4.21 (dd, 12.0, 5.5)	3.68 (dd, 12.0, 5.0)	3.66 (dd, 12.0, 5.0)	3.67*	3.71*
	Glc	Glc	Glc		Glc
H-1″	4.73 (d, 8.0)	4.71 (d. 8.0)	4.56 (d, 8.0)	—	4.54 (d, 8.0)
-2″	3.32*	3.32*	3.29*	—	3.35 (dd, 9.0, 8.0)
-3″	3.42 (t, 9.0)	3.42 (t, 8.0)	3.42*	—	3.46 (t, 9.0)
-4″	3.31*	3.28*	3.42*	—	3.29*
-5″	3.71 (m)	3.73*	3.42*	—	3.72*
-6″	4.50 (2H, *)	4.55 (dd, 12.0, 9.0)	3.93*	—	4.56 (dd, 12.0, 9.0)
	—	4.46 (dd, 12.0, 2.0)	3.80 (dd, 12.0, 4.0)	—	4.45 (dd, 12.0, 2.0)
	Glc	Xyl			
H-1‴	4.71 (d, 8.0)	4.64 (d, 8.0)	—	—	—
-2‴	3.08 (t, 8.0)	3.03 (dd, 9.0, 8.0)	—	—	—
-3‴	3.28*	3.23 (t, 9.0)	—	—	—
-4‴	3.26*	3.45 (m)	—	—	—
-5‴	3.24*	3.76 (dd, 11.5, 5.0)	—	—	—
	—	3.13 (t, 11.0)	—	—	—
-6‴	3.82 (dd, 12.0, 2.0)	—	—	—	—
	3.63 (dd, 12.0, 5.0)	—	—	—	—
7-*O*-Sugar					
			Rha	Glc	Rha
H-1⁗	—	—	5.57 (d, 1.5)	5.24 (d-like, 7.5)	5.55 (d, 1.5)
-2⁗	—	—	4.03 (dd, 3.5, 1.5)	3.73*	4.04 (dd, 3.5, 1.5)
-3⁗	—	—	3.83 (dd, 9.5, 3.5)	3.73*	3.84 (dd, 9.5, 3.5)
-4⁗	—	—	3.48 (t, 9.5)	3.46 (t, 9.0)	3.49 (t, 9.5)
-5⁗	—	—	3.61 (dq, 9.5, 6.0)	3.54 (m)	3.65*
-6⁗	—	—	1.21 (d, 6.0)	3.92 (dd, 12.0, 2.0)	1.29 (d, 6.0)
	—	—	—	3.71*	—
				Glc	
H-1⁗′	—	—	—	4.67 (d, 8.0)	—
-2⁗′	—	—	—	3.26 (t, 8.0)	—
-3⁗′	—	—	—	3.40 (t, 8.0)	—
-4⁗′	—	—	—		—
-5⁗′	—	—	—	3.26*	—
-6⁗′	—	—	—	3.67 (dd, 12.0, 4.0)	—
	—	—	—	3.61 (dd, 12.0, 2.0)	—
Ester moieties					
(R_2) H-β	6.16 (d, 16.0)	—	—	—	—
-γ	7.49 (d, 16.0)	—	—	—	—
-2,6	7.27 (brd, 8.5)	—	—	—	—
-3,5	6.68 (brd, 8.5)	—	—	—	—
(R_3) H-β′	6.19 (d, 16.0)	6.22 (d, 16.0)	—	—	6.24 (d, 16.0)
-γ′	7.50 (d, 16.0)	7.53 (d, 16.0)	—	—	7.53 (d, 16.0)
-2′,6′	7.04 (brd, 8.5)	7.07 (brd, 8.5)	—	—	7.08 (brd, 8.5)
-3′,5′	6.38 (brd, 8.5)	6.37 (brd, 8.5)	—	—	6.35 (brd, 8.5)

Table 2. (Continued)

	21	22	23	26	27
Aglycone moiety					
H-6	6.34 (d, 2.0)	6.43 (d, 2.0)	6.38 (d, 2.0)	6.38 (d, 2.0)	6.33 (d, 2.0)
-8	6.41 (d, 2.0)	6.57 (d, 2.0)	6.42 (d, 2.0)	6.54 (d, 2.0)	6.37 (d, 2.0)
-2′,6′	7.69 (brd, 9.0)	7.78 (brd, 9.0)	7.69 (brd, 9.0)	7.76 (brd, 9.0)	7.67 (brd, 8.5)
-3′,5′	6.92 (brd, 9.0)	6.96 (brd, 9.0)	6.93 (brd, 9.0)	6.96 (brd, 9.0)	6.92 (brd, 8.5)
3-*O*-Sugars					
	Rha	Rha	Rha	Rha	Rha
H-1	5.82 (d, 1.5)	5.84 (d, 1.5)	5.82 (brs)	5.73 (d, 1.5)	5.69 (d, 1.5)
-2	4.55*	4.51 (dd, 3.5, 1.5)	4.55*	4.45 (dd, 3.0, 1.5)	4.49 (dd, 3.5, 1.5)
-3	3.88 (dd, 9.5, 3.5)	3.82 (dd, 9.5, 3.5)	3.87 (dd, 9.5, 3.5)	4.07 (dd, 10.0, 3.0)	4.13 (dd, 9.5, 3.5)
-4	3.53 (t, 9.5)	3.49 (t, 9.5)	3.53 (t, 9.5)	3.63 (t, 10.0)	3.67 (t, 9.5)
-5	3.44*	3.22*	3.40*	3.24*	3.48*
-6	1.01 (d, 6.0)	0.92 (d, 6.0)	1.00 (d, 6.0)	0.91 (d, 6.0)	0.99 (d, 6.0)
	Glc	Glc	Glc	Glc	Glc
H-1′	4.56 (d, 8.0)	4.57 (d, 8.0)	4.55 (d, 8.5)	4.55 (d, 8.0)	4.52 (d, 8.0)
-2′	3.26 (dd, 9.0, 8.0)	3.21 (t, 9.0)	3.26 (t, 8.5)	3.22 (dd, 9.0, 8.0)	3.27 (dd, 9.0, 8.0)
-3′	3.42 (t, 9.0)	3.38*	3.43 (t, 8.5)	3.40 (t, 9.0)	3.42 (t, 9.0)
-4′	3.33*	3.33*	3.33*	3.36*	3.32*
-5′	3.53*	3.33*	3.53*	3.32*	3.47*
-6′	4.53*	3.83 (dd, 12.0, 2.0)	4.53*	3.80 (dd, 12.0, 2.0)	4.49 (dd, 12.0, 2.5)
	4.20 (dd, 12.0, 6.0)	3.71*	4.21 (dd.12.0, 6.0)	3.70 (dd, 12.0, 5.0)	4.19 (dd, 12.0, 6.0)
	Glc	Glc	Glc	Glc	Glc
H-1″	4.58 (d, 8.0)	4.54 (d, 8.0)	4.58 (d, 8.0)	4.72 (d, 8.0)	4.75**
-2″	3.36 (dd, 9.0, 8.0)	3.36 (dd, 9.0, 8.0)	3.36 (dd, 9.0, 8.0)	3.32*	3.33*
-3″	3.46 (t, 9.0)	3.46 (t, 9.0)	3.46 (t, 9.0)	3.43 (t, 9.0)	3.43 (t, 9.0)
-4″	3.30*	3.29 (t, 9.0)	3.31*	3.28*	3.29*
-5″	3.71*	3.73*	3.72 (m)	3.74*	3.72 (m)
-6″	4.53*	4.56*	4.53*	4.59 (dd, 12.0, 9.0)	4.54 (dd, 12.0, 9.0)
	4.48 (dd, 12.0, 2.5)	4.45 (dd, 12.0, 2.0)	4.48 (dd, 12.0, 2.0)	4.42 (dd, 12.0, 2.0)	4.44 (dd, 12.0, 2.0)
				Xyl	Xyl
H-1‴	—	—	—	4.65 (d, 8.0)	4.68 (d, 8.0)
-2‴	—	—	—	3.03 (dd, 9.0, 8.0)	3.06 (dd, 9.0, 8.0)
-3‴	—	—	—	3.24 (t, 9.0)	3.26 (t, 9.0)
-4‴	—	—	—	3.43*	3.45*
-5‴	—	—	—	3.76 (dd, 11.5, 5.5)	3.78 (dd, 11.5, 5.5)
	—	—	—	3.13 (t, 11.5)	3.15 (t, 11.5)
-6‴	—	—	—	—	—
	—	—	—	—	—
7-*O*-Sugar					
	Rha	Glc	Glc	Rha	Rha
H-1⁗	5.51 (d, 1.5)	5.07 (d-like, 8.0)	5.05 (d-like, 8.0)	5.56 (d, 2.0)	5.51 (d, 1.5)
-2⁗	4.04 (dd, 3.5, 1.5)	3.50*	3.52*	4.04 (dd, 3.5, 2.0)	4.06 (dd, 3.5, 1.5)
-3⁗	3.84 (dd, 9.5, 3.5)	3.51*	3.52*	3.84 (dd, 9.5, 3.5)	3.85 (dd, 9.5, 3.5)
-4⁗	3.49 (t, 9.5)	3.40*	3.42*	3.49 (t, 9.5)	3.49 (t, 9.5)
-5⁗	3.68 (dq, 9.5, 6.0)	3.55 (m)	3.55*	3.66 (m)	3.68*
-6⁗	1.30 (d, 6.0)	3.96 (dd, 12.0, 2.5)	3.98 (dd, 12.0, 2.0)	1.29 (d, 6.0)	1.30 (d, 6.0)
	—	3.71*	3.75 (dd, 12.0, 6.0)	—	—
H-1⁗′	—	—	—	—	—
-2⁗′	—	—	—	—	—
-3⁗′	—	—	—	—	—
-4⁗′	—	—	—	—	—
-5⁗′	—	—	—	—	—
-6⁗′	—	—	—	—	—
	—	—	—	—	—
Ester moieties					
(R_2) H-β	6.10 (d, 16.0)	—	6.12 (d, 16.0)	—	6.12 (d, 16.0)
-γ	7.67 (d, 16.0)	—	7.48 (d, 16.0)	—	7.47 (d, 16.0)
-2,6	7.24 (brd, 9.0)	—	7.23 (brd, 8.5)	—	7.26 (brd, 9.0)
-3,5	6.68 (brd, 9.0)	—	6.68 (brd, 8.5)	—	6.67 (brd, 9.0)
(R_3) H-β′	6.20 (d, 16.0)	6.25 (d, 16.0)	6.21 (d, 16.0)	6.20 (d, 16.0)	6.16 (d, 16.0)
-γ′	7.50 (d, 16.0)	7.53 (d, 16.0)	7.50 (d, 16.0)	7.50 (d, 16.0)	7.46 (d, 16.0)
-2′,6′	7.05 (brd, 9.0)	7.07 (brd, 8.5)	7.04 (brd, 8.5)	7.03 (brd, 8.5)	6.98 (brd, 9.0)
-3′,5′	6.35 (brd, 9.0)	6.36 (brd, 8.5)	6.37 (brd, 8.5)	6.32 (brd, 8.5)	6.32 (brd, 9.0)

Table 2. (Continued)

	28	29	30
Aglycone moiety			
H-6	6.36 (d, 2.0)	6.36 (d, 2.0)	6.44 (d, 2.0)
-8	6.38 (d, 2.0)	6.39 (d, 2.0)	6.41 (d, 2.0)
-2′,6′	7.67 (brd, 9.0)	7.68 (brd, 9.0)	7.71 (brd, 9.0)
-3′,5′	6.92 (brd, 9.0)	6.92 (brd, 9.0)	6.93 (brd, 9.0)
3-*O*-Sugars			
	Rha	Rha	Rha
H-1	5.68 (d, 1.5)	5.69 (brs)	5.81 (brs)
-2	4.48 (dd, 3.5, 1.5)	4.49 (brd, 3.5)	4.56*
-3	4.12 (dd, 9.5, 3.5)	4.12 (dd, 9.5, 3.5)	3.86 (dd, 9.5, 3.5)
-4	3.66 (t, 9.5)	3.76 (t, 9.5)	3.52*
-5	3.48*	3.48*	3.39*
-6	0.99 (d, 6.0)	1.04 (d, 6.0)	1.00 (d, 6.0)
	Glc	Glc	Glc
H-1′	4.51 (d, 8.0)	4.53 (d, 8.0)	4.57 (d, 8.0)
-2′	3.26 (dd, 9.0, 8.0)	3.26 (dd, 9.0, 8.0)	3.26 (dd, 9.0, 8.0)
-3′	3.42 (t, 9.0)	3.42 (t, 9.0)	3.44 (t, 9.0)
-4′	3.32*	3.32*	3.34*
-5′	3.47*	3.48*	3.54*
-6′	4.50 (dd, 12.0, 2.0)	4.51 (dd, 12.0, 2.0)	4.54*
	4.19 (dd, 12.0, 6.0)	4.20 (dd, 12.0, 6.0)	4.21 (dd, 12.0, 6.0)
	Glc	Glc	Glc
H-1″	4.76**	4.75**	4.58 (d, 8.0)
-2″	3.33 (dd, 9.0, 8.0)	3.33*	3.36 (dd, 9.0, 8.0)
-3″	3.42 (t, 9.0)	3.43 (t, 9.0)	3.46 (t, 9.0)
-4″	3.29*	3.29*	3.31*
-5″	3.73 (m)	3.73*	3.71*
-6″	4.55 (dd, 12.0, 9.0)	4.56 (dd, 12.0, 9.0)	4.52 (dd, 12.0, 8.0)
	4.43 (dd, 12.0, 2.0)	4.43 (dd, 12.0, 2.0)	4.48 (dd, 12.0, 2.0)
	Xyl	Glc	
H-1‴	4.68 (d, 8.0)	4.72 (d, 8.0)	—
-2‴	3.06 (dd, 9.0, 8.0)	3.08 (t, 8.0)	—
-3‴	3.25 (t, 9.0)	3.31*	—
-4‴	3.46*	3.24*	—
-5‴	3.78 (dd, 11.5, 5.5)	3.24*	—
	3.14 (t, 11.5)	—	—
-6‴	—	3.82 (dd, 12.0, 2.0)	—
	—	3.63 (dd, 12.0, 5.0)	—
7-*O*-Sugar			
	Glc	Glc	Glc
H-1⁗	5.05 (d-like, 8.0)	5.05 (d-like, 8.0)	5.05 (d-like, 8.0)
-2⁗	3.51*	3.52*	3.52*
-3⁗	3.51*	3.52*	3.52*
-4⁗	3.42*	3.42*	3.52*
-5⁗	3.55*	3.55*	3.76*
-6⁗	3.98 (dd, 12.0, 2.5)	3.98 (dd, 12.0, 2.5)	4.40 (dd, 11.5, 5.0)
	3.75 (dd, 12.0, 6.0)	3.75*	3.86 (dd, 11.5, 2.0)
			α-Glc
H-1⁗′	—	—	4.90 (d, 4.0)
-2⁗′	—	—	3.40 (dd, 9.0, 4.0)
-3⁗′	—	—	3.37 (t, 9.0)
-4⁗′	—	—	3.31*
-5⁗′	—	—	3.66*
-6⁗′	—	—	3.77*
	—	—	3.64*
Ester moieties			
(R_2) H-*β*	6.14 (d, 16.0)	6.16 (d, 16.0)	6.13 (d, 16.0)
-*γ*	7.46 (d, 16.0)	7.46 (d, 16.0)	7.48 (d, 16.0)
-2,6	7.24 (brd, 8.5)	7.24 (brd, 8.5)	7.25 (brd, 8.5)
-3,5	6.67 (brd, 8.5)	6.67 (brd, 8.5)	6.68 (brd, 8.5)
(R_3) H-*β*′	6.16 (d, 16.0)	6.17 (d, 16.0)	6.22 (d, 16.0)
-*γ*′	7.47 (d, 16.0)	7.48 (d, 16.0)	7.51 (d, 16.0)
-2′,6′	6.97 (brd, 8.5)	6.97 (brd, 8.5)	7.06 (brd, 8.5)
-3′,5′	6.33 (brd, 8.5)	6.33 (brd, 8.5)	6.38 (brd, 8.5)

Measured in MeOH-d_4 solution at 35°C. *: Overlapped with other signals. **: Overlapped with the H_2O signal. Data of the ester moieties may be interchangeable in each column. Rha:*α*-L-rhamnopyranose, Qui: *β*-D-quinovopyranose, Glc: *β*-D-glucopyranose, *α*-Glc: *α*-D-glucopyranose, Xyl: *β*-D-xylopyranose.

(MeOH) nm (log ε): 266 (4.34), 327 (sh), 344 (4.18).

Ternatumoside X (**20**): Yellow amorphous powder. $[\alpha]_D^{18}$ −41 (c=0.39, MeOH). FAB-MS m/z: 1071 $[M+Na]^+$. HR-FAB-MS m/z: 1071.2996 (Calcd for $C_{48}H_{56}O_{26}Na$: 1071.2958). UV λ_{max} (MeOH) nm (log ε): 220 (sh), 269 (4.29), 316 (4.34).

Compound **21**: Yellow amorphous powder. $[\alpha]_D^{19}$ −65 (c=0.39, MeOH). FAB-MS m/z: 1217 $[M+Na]^+$, 1195 $[M+H]^+$. HR-FAB-MS m/z: 1217.3307 (Calcd for $C_{57}H_{62}O_{28}Na$: 1217.3325). UV λ_{max} (MeOH) nm (log ε): 226 (4.55), 271 (4.51), 314 (4.70).

Ternatumoside XI (**22**): Yellow amorphous powder. $[\alpha]_D^{24}$ −22 (c=1.06, MeOH). FAB-MS m/z: 1087 $[M+Na]^+$, 1065 $[M+H]^+$. HR-FAB-MS m/z: 1087.2911 (Calcd for $C_{48}H_{56}O_{27}Na$: 1087.2907). UV λ_{max} (MeOH) nm (log ε): 269 (4.42), 316 (4.48).

Ternatumoside XII (**23**): Yellow amorphous powder. $[\alpha]_D^{20}$ −30 (c=1.62, MeOH). FAB-MS m/z: 1233 $[M+Na]^+$. HR-FAB-MS m/z: 1233.3320 (Calcd for $C_{57}H_{62}O_{29}Na$: 1233.3274). UV λ_{max} (MeOH) nm (log ε): 225 (4.44), 271 (4.38), 314 (4.57).

Ternatumoside XIII (**26**): Yellow amorphous powder. $[\alpha]_D^{24}$ −76 (c=0.52, MeOH). FAB-MS m/z: 1203 $[M+Na]^+$. HR-FAB-MS m/z: 1203.3372 (Calcd for $C_{53}H_{64}O_{30}Na$: 1203.3381). UV λ_{max} (MeOH) nm (log ε): 269 (4.45), 315 (4.50).

Ternatumoside XIV (**27**): Yellow amorphous powder. $[\alpha]_D^{20}$ −72 (c=0.59, MeOH). FAB-MS m/z: 1349 $[M+Na]^+$. HR-FAB-MS m/z: 1349.3755 (Calcd for $C_{62}H_{70}O_{32}Na$: 1349.3748). UV λ_{max} (MeOH) nm (log ε): 225 (4.53), 271 (4.48), 314 (4.67).

Ternatumoside XV (**28**): Yellow amorphous powder. $[\alpha]_D^{26}$ −43 (c=1.08, MeOH). FAB-MS m/z: 1365 $[M+Na]^+$. HR-FAB-MS m/z: 1365.3710 (Calcd for $C_{62}H_{70}O_{33}Na$: 1365.3697). UV λ_{max} (MeOH) nm (log ε): 226 (4.54), 271 (4.49), 314 (4.67).

Ternatumoside XVI (**29**): Yellow amorphous powder. $[\alpha]_D^{26}$ −39 (c=1.12, MeOH). FAB-MS m/z: 1395 $[M+Na]^+$. HR-FAB-MS m/z: 1395.3812 (Calcd for $C_{63}H_{72}O_{34}Na$: 1395.3803). UV λ_{max} (MeOH) nm (log ε): 225 (4.52), 271 (4.47), 314 (4.65).

Ternatumoside XVII (**30**): Yellow amorphous powder. $[\alpha]_D^{26}$ −31 (c=0.75, MeOH). FAB-MS m/z: 1395 $[M+Na]^+$. HR-FAB-MS m/z: 1395.3833 (Calcd for $C_{63}H_{72}O_{34}Na$: 1395.3803). UV λ_{max} (MeOH) nm (log ε): 226 (4.52), 271 (4.46), 314 (4.65).

The ^{13}C- and ^1H-NMR spectroscopic data for compounds **4**, **6**, **8**–**12**, **18**–**23**, **26**–**29**, and **30** were presented in Tables 1 and 2.

Acid Hydrolysis of Compounds 4, 6, 10, 18 and 19 Compounds **4**, **6**, **10**, **18** and **19** (*ca.* 1 mg) were dissolved in 2 M HCl (200 μL). The solutions were heated at 100°C for 1 h. After hydrolysis, this reaction mixture was diluted with H_2O and extracted with EtOAc. The EtOAc layer was concentrated dry, and the residue from each compound was analyzed using HPLC through a comparison with the authentic sample. HPLC conditions: column, YMC-ODS-AM 4.6 mm i.d.×25 cm; flow rate, 1.0 mL/min; 35% MeCN in water; t_R, 14.0 min (kaempferol: The authentic sample was provided by Prof. T. Miyase.). Kaempferol was detected in all compounds. The H_2O layer was neutralized with an Amberlite IRA-60E column, and the eluate was concentrated dry. The residue was stirred with D-cysteine methyl ester hydrochloride, hexamethyldisilazane and trimethylsilylchloride in pyridine using the same procedures as in previous reports.[21,22] After the reactions, the supernatant was subjected to GC. GC conditions: column, TC-1 (GL Science Inc.) 0.25 mm i.d.×30 m; carrier gas, N_2; column temperature, 230°C; t_R, 22.8 min (D-glucose (Tokyo Kasei Kogyo Co., Ltd.)), 22.0 min (L-glucose), 15.4 min (L-rhamnose (Tokyo Kasei Kogyo Co., Ltd.)), 15.0 min (D-rhamnose), 13.2 min (D-xylose (Tokyo Kasei Kogyo Co., Ltd.)), 12.4 min (L-xylose), 14.8 min (D-quinovose (Sigma Chem. Co.)), 14.3 min (L-quinovose). The t_Rs for L-glucose, D-rhamnose, L-xylose, and L-quinovose were obtained from their enantiomers (D-glucose+L-cysteine, L-rhamnose+L-cysteine, D-xylose+L-cysteine, and D-quinovose+L-cysteine). L-Rhamnose was found in all compounds, and D-glucose was identified in **6**, **10**, **18** and **19**. D-Quinovose was detected in **4**.

Alkaline and Acid Hydrolysis of Compounds 8, 9, 11, 12, 20–23, 26–29, and 30 Compounds **8**, **9**, **11**, **12**, **20**–**23**, **26**–**29**, and **30** were dissolved in 0.05 M NaOH (100 μL), and stirred at room temperature for 3–4 h under an N_2 atmosphere. After the reactions, the mixture was neutralized with an Amberlite IR-120B column with the eluate concentrated dry. The residue was partitioned between EtOAc and H_2O, and both layers were concentrated dry. The residue from the EtOAc layer was analyzed using HPLC through a comparison with the authentic sample. HPLC conditions: column, YMC-ODS-AM 4.6 mm i.d.×25 cm; flow rate, 1.0 mL/min; 17.5% MeCN in water+0.05% trifluoroacetic acid (TFA); t_R, 14.0 min [(*trans*)-*p*-coumaric acid (Tokyo Kasei Kogyo Co., Ltd.)]. (*trans*)-*p*-Coumaric acid was detected in all compounds. The residues from the H_2O layers of compounds **8**, **9**, **11**, **20**, and **21** were also analyzed using HPLC through a comparison with compounds **7**, **10** and **18**. HPLC conditions: column, YMC-ODS-AM 4.6 mm i.d.×25 cm; flow rate, 1.0 mL/min; 17.5% MeCN; t_R, 11.2 min (**18**), 19.0 min (**10**), 25.2 min (**7**). **7** was detected in **8** and **9**, and **10** was found in **11**. **18** was identified in **20** and **21**. Other residues were hydrolyzed with 2 M HCl, and the procedures were described above. Kaempferol, L-rhamnose, and D-glucose were detected in all compounds. D-Xylose was found in **12**, **26**, **27**, and **28**.

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