Triterpenoid Saponins from the Fruits of *Ternstroemia japonica*

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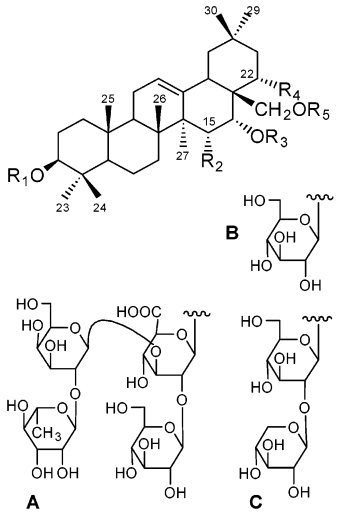
Three new triterpenoidal monodesmosides (**1**−**3**) and three new triterpenoidal bisdesmosides (**4**−**6**), together with two known saponins (**7** and **8**), were isolated from the fresh fruits of *Ternstroemia japonica*. The structures of **1**−**6** (ternstroemiasides A−F) were elucidated on the basis of spectral analysis and chemical degradation.

Ternstroemia japonica Thunb. (Theaceae) is a tall tree that grows in Korea, Japan, Taiwan, the People's Republic of China, and the Philippines.[1] Its fruits have been used for the treatment of chest pain and numbness in traditional Chinese medicine.[2] An aldehydic carotenoid and triterpenes such as oleanolic acid, primulagenin A, camelliagenin A, and A_1-barrigenol have been reported from this plant.[3] Herein, we describe the isolation and structure elucidation of six new oleanane-type saponins (**1**−**6**) from the fresh fruits of the plant. These saponins all possess an α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→2)]-β-D-glucuronopyranosyl tetrasaccharide unit at C-3 of the aglycon. Additional sugar moieties attached at C-28 of the three bisdesmosides (**4**−**6**) were β-D-glucopyranosyl (**4** and **5**) and a β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl unit (**6**). The aglycons of the saponins were identified as camelliagenin A (**1a** from **1**), 16-*O*-acetyl camelliagenin A (**2a** from **2**), 3β,15α,16α,28-tetrahydroxyolean-12-ene (**3a** from **3** and **4**), 16-*O*-acetyl primulagenin A (**5a** from **5**), primulagenin A (**6a** from **6** and **7**), and A_1-barrigenol (**8a** from **8**).



	R_1	R_2	R_3	R_4	R_5
1	A	H	H	OH	H
1a	H	H	H	OH	H
2	A	H	Ac	OH	H
2a	H	H	Ac	OH	H
3	A	OH	H	H	H
3a	H	OH	H	H	H
4	A	OH	H	H	B
5	A	H	Ac	H	B
5a	H	H	Ac	H	H
6	A	H	H	H	C
6a	H	H	H	H	H
7	A	H	H	H	H
8	A	OH	H	OH	H
8a	H	OH	H	OH	H

Results and Discussion

A crude saponin mixture obtained from the fresh fruits of *T. japonica* afforded saponins **1**−**8** after various chromatographic separations.

Ternstroemiaside A (**1**) was obtained as colorless needles. The molecular formula was established as $C_{54}H_{88}O_{24}$ on the basis of the analysis of its NMR and MS data. LRFABMS of **1** gave a $[M + K]^+$ ion peak at *m/z* 1159 and a $[M + Na]^+$ ion peak at *m/z* 1143. The molecular formula was further confirmed by the $[M + H]^+$ ion at *m/z* 1121.5703 (calcd for $C_{54}H_{89}O_{24}$, 1121.5738) in the HRESIMS. The IR spectrum showed the presence of carboxyl (1734 cm^{-1}) and hydroxyl (3390 cm^{-1}) groups. By comparison of the NMR data (Tables 1−3) with those reported,[4] an olean-12-ene triterpene with a tetrasaccharide unit could be deduced. The two oxymethylene proton signals at δ 3.52 and 3.20, which correlated with the carbon signal at δ 70.3 in the HMQC spectrum, were diagnostic for H-28. The oxymethine proton signal at δ 4.36, which correlated with C-15 (δ 35.0) and C-28 (δ 70.3) in the HMBC spectrum, could be assigned to H-16. The correlation between H-16 and H-28, in the NOESY spectrum, suggested an α-configuration of the hydroxyl group at C-16, which was also supported by the splitting pattern of H-16 (br s). The proton signal at δ 4.03 could be assigned to H-22 on the basis of its correlations with C-16, C-18, C-21, and C-28 in the HMBC spectrum. The correlation between H-22 and H-30 in the NOESY spectrum indicated an α-configuration of the hydroxyl group at C-22, which was corroborated by the splitting pattern of H-22 (dd, $J = 12.5$, 6.0 Hz). Correlations of H-3 (δ 3.19) with H-1_{ax} (δ 1.05), H-5 (δ 0.80), and H-23 (δ 1.09) in the NOESY spectrum indicated a β-configuration of the hydroxyl group at C-3. Thus, the aglycon of **1** could be identified as camelliagenin A.[3b] The presence of camelliagenin A was confirmed by methanolysis of **1** followed by TLC comparison of the hydrolysate with authentic sample.

The ^{13}C NMR spectrum of the sugar portion of **1** showed two oxymethylene signals (δ 62.8 and 63.6), one methyl signal (δ 17.9), four anomeric signals (δ 100.9, 102.2, 102.6, and 105.9), and one carboxylic signal (δ 172.3). Four anomeric proton signals (δ 4.52, 4.87, 5.17, and 5.28) and one methyl doublet (δ 1.28, $J = 6.0$ Hz) were observed in

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Table 1. ^{1}H NMR Data of the Aglycons of Compounds **1**−**6** (CD_3OD, 500 MHz)[a]

position	1	2	3	4	5	6
1	1.66 (m)	1.63 (m)	1.65 (m)	1.67 (m)	1.68 (m)	1.63 (m)
	1.05 (m)	1.02 (m)	1.04 (m)	1.00 (m)	1.03 (m)	1.00 (m)
2	1.87 (m)	1.89 (m)	1.89 (m)	1.86 (m)	1.89 (m)	1.87 (m)
	1.75 (m)	1.74 (m)	1.75 (m)	1.74 (m)	1.75 (m)	1.75 (m)
3	3.19 (m)	3.18 (dd, 12.0, 4.5)	3.20 (dd, 12.5, 5.0)	3.22 (dd, 12.0, 5.5)	3.22 (m)	3.19 (m)
4						
5	0.80 (d, 10.5)	0.78 (d, 11.5)	0.79 (d, 11.0)	0.80 (br d, 11.0)	0.81 (br d, 12.0)	0.80 (br d, 13.0)
6	1.60 (m)	1.57 (m)	1.54 (m)	1.56 (m)	1.58 (br d, 10.5)	1.58 (m)
	1.36 (m)	1.41 (m)	1.34 (m)	1.31 (m)	1.43 (m)	1.44 (m)
7	1.63 (m)	1.55 (m)	1.75 (m)	1.76 (m)	1.55 (m)	1.59 (m)
	1.40 (m)	1.35 (m)			1.36 (m)	1.47 (m)
8						
9	1.67	1.64 (dd, 9.5, 3.0)	1.58 (dd, 10.8, 6.5)	1.58 (dd, 10.0, 7.0)	1.68 (m)	1.60 (m)
10						
11	1.90 (m)	1.91 (m)	1.90 (m)	1.89 (m)	1.93 (m)	1.89 (m)
12	5.27 (t, 3.0)	5.33 (t, 3.0)	5.33 (t, 3.0)	5.33 (t, 3.5)	5.35 (t, 3.5)	5.28 (m)
13						
14						
15	1.92 (m)	1.91 (dd, 12.5, 3.5)	3.96 (m)	4.01 (d, 4.0)	2.03 (dd, 11.5, 4.5)	1.94 (m)
	1.36 (dd, 12.0, 4.0)	1.47 (br d, 12.5)			1.39 (br d, 15.0)	1.37 (dd, 15.0, 6.5)
16	4.36 (br s)	5.48 (br s)	3.80 (d, 3.0)	3.98 (d, 4.0)	5.36 (t, 3.5)	4.08 (m)
17						
18	2.12 (dd, 14.0, 4.0)	2.16 (dd, 13.0, 4.0)	2.04 (dd, 14.5, 4.0)	2.00 (dd, 13.0, 4.0)	2.10 (m)	1.87 (m)
19	1.01 (m)	1.11 (m)	0.99 (m)	0.95 (m)	1.13 (br d, 10.5)	1.00 (m)
	2.39 (t, 13.5)	2.25 (t, 13.0)	2.24 (t, 13.0)	2.26 (t, 13.0)	2.17 (t, 13.0)	2.10 (t, 13.5)
20						
21	2.03 (t, 12.5)	1.67 (t, 12.5)	1.86 (t, 12.5)	1.82 (dt, 13.0, 4.5)	1.47 (dt, 13.0, 5.0)	1.59 (m)
	1.43 (m)	1.45 (br d, 12.5)	1.17 (m)	1.18 (td, 13.0, 5.0)	1.22 (td, 11.0, 2.0)	1.19 (m)
22	4.03 (dd, 12.5, 6.0)	4.04 (dd, 12.5, 4.5)	1.78 (m)	1.92 (m)	1.76 (br d, 13.5)	1.69 (m)
			1.62 (dd, 12.5, 6.0)	1.63 (m)	1.68 (m)	1.57 (m)
23	1.09 (s)	1.07 (s)	1.08 (s)	1.08 (s)	1.09 (s)	1.08 (s)
24	0.89 (s)	0.89 (s)	0.89 (s)	0.89 (s)	0.91 (s)	0.89 (s)
25	0.98 (s)	0.98 (s)	0.99 (s)	0.99 (s)	1.00 (s)	0.98 (s)
26	0.95 (s)	0.96 (s)	1.02 (s)	1.03 (s)	1.00 (s)	0.96 (s)
27	1.44 (s)	1.31 (s)	1.33 (s)	1.34 (s)	1.33 (s)	1.31 (s)
28	3.52 (d, 10.0)	3.60 (d, 11.0)	3.32 (d, 11.0)	3.47 (d, 10.0)	3.56 (d, 10.0)	3.64 (m)
	3.20 (d, 10.0)	3.27 (d, 11.0)	3.09 (d, 11.0)	3.33 (d, 10.0)	3.39 (d, 10.0)	3.14 (d, 10.0)
29	0.90 (s)	0.95 (s)	0.86 (s)	0.86 (s)	0.93 (s)	0.89 (s)
30	0.96 (s)	0.98 (s)	0.91 (s)	0.91 (s)	0.96 (s)	0.92 (s)
CO*Me*		2.04 (s)			2.09 (s)	

[a] Multiplicities and coupling constants are in parentheses.

the ^{1}H NMR spectrum. These observations and the TLC analysis of the acid hydrolysate revealed the presence of glucuronic acid (glcA), glucose (glc), galactose (gal), and rhamnose (rha). The identity of each sugar was confirmed by HPLC analysis.[5] The sequence of this tetrasaccharide was determined by the analyses of DEPT, COSY, HMQC, HMBC, and NOESY data. The significant glycosidation shift of the C-3 signal to δ 92.4 and the cross-peak between C-3 of the aglycon (δ 92.4) and H-1 of glcA (δ 4.52) in the HMBC spectrum indicated that glcA was connected to C-3 of the aglycon. The linkage of the terminal glc at C-2 of glcA was indicated by the cross-peak between H-1 of glc (δ 4.87) and C-2 of glcA (δ 79.1) in the HMBC spectrum. Similarly, the linkages of the terminal rha at C-2 of gal and of the internal gal at C-3 of glcA were indicated by the correlations between H-1 of rha (δ 5.28) and C-2 of gal (δ 76.0) and between H-1 of gal (δ 5.17) and C-3 of glcA (δ 81.1), respectively. The coupling constants of the anomeric protons of glcA (7.5 Hz), glc (7.0 Hz), and gal (7.5 Hz) along with the correlations between H-1 and H-5 of glcA, glc, and gal in the NOESY experiments indicated β-configurations for these sugars. The strong HMBC correlations between the anomeric proton (δ 5.28) and C-3 (δ 72.3) and between the anomeric proton and C-5 (δ 70.3) and the NOESY cross-peak between H-1 and H-2 indicated an α-configuration for rha.[6,7] Common D-configurations for gal, glc, and glcA and the common L-configuration for rha were determined by GLC analysis of the thiazolidine derivative of each sugar.[8] Thus, the structure of **1** was established as 3-*O*-{α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→2)]-β-D-glucuronopyranosyl}-camelliagenin A.

Ternstroemiaside B (**2**) was isolated as colorless needles. In the LRFABMS, it showed a $[M + K]^+$ ion peak at *m*/*z* 1201 and a $[M + Na]^+$ ion peak at *m*/*z* 1185, indicating the molecular formula of $C_{56}H_{90}O_{25}$. Comparison of the NMR data with those of **1** and TLC analysis of the acid hydrolysate indicated that they share the same sugar moiety. In the ^{1}H NMR spectrum of **2**, an additional acetoxy methyl singlet at δ 2.04 was observed and the signal of H-16 shifted downfield to δ 5.48. The ^{13}C NMR spectrum showed the upfield shifts of C-15 (−3.5 ppm) and C-17 (−0.9 ppm) and showed two additional signals at δ 22.2 and 171.5. A correlation between H-16 (δ 5.48) and carbonyl carbon (δ 171.5) was observed in the HMBC spectrum, implying that acetylation of the hydroxyl group was apparent at C-16.[4,9−11] The stereochemistries of the sugars were assumed to be the same as those of **1**. Thus, the structure of **2** was defined as 3-*O*-{α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→2)]-β-D-glucuronopyranosyl}-16-*O*-acetylcamelliagenin A.

Ternstroemiaside C (**3**) was isolated as colorless needles. It showed an identical molecular mass to that of **1** in the LRFABMS. The NMR data and TLC analysis of the hydrolysate of **3** indicated that it shares the same sugar moiety as that of **1**. The only difference was the presence of an OH-15α unit in the aglycon instead of an OH-22α as

Table 2. ^{13}C NMR Data of the Aglycons of Compounds **1**−**6** (CD_3OD, 50 MHz)

position	1	2	3	4	5	6
1	40.0	39.9	40.1	40.0	39.9	39.9
2	27.0	27.0	27.1	27.1	27.0	27.0
3	92.4	91.9	92.4	92.3	92.2	92.3
4	40.6	40.5	40.5	40.5	40.6	40.6
5	57.0	56.8	56.7	56.6	56.9	57.0
6	19.3	19.2	19.6	19.6	19.2	19.3
7	34.0	33.9	37.3	37.2	33.9	34.0
8	41.0	41.1	42.2	42.7	41.1	41.3
9	48.1	48.0	48.3	48.3	47.8	48.4
10	37.8	37.8	38.0	37.9	37.8	37.8
11	24.7	24.5	24.7	24.7	24.6	24.5
12	124.0	124.9	125.2	125.3	125.0	123.5
13	144.3	142.3	146.0	145.8	143.6	144.5
14	42.8	42.5	48.9	48.5	42.3	42.7
15	35.0	31.5	68.4	68.4	31.9	35.5
16	69.3	72.5	78.7	78.0	78.0	74.7
17	45.3	44.4	41.5	40.5	39.6	41.4
18	42.8	42.6	44.1	44.5	43.5	44.9
19	48.5	48.0	48.3	48.3	48.3	48.1
20	32.3	32.2	31.7	31.6	31.6	31.2
21	46.0	45.0	37.4	37.2	37.0	35.7
22	74.7	73.8	31.1	32.0	31.9	27.4
23	28.4	28.3	28.4	28.4	28.3	28.3
24	17.0	16.9	17.0	17.0	16.9	16.9
25	16.2	16.1	16.3	16.4	16.2	16.4
26	17.4	17.2	18.0	18.0	17.5	18.1
27	27.6	27.4	20.7	20.7	27.3	27.7
28	70.3	69.9	70.3	78.1	78.8	78.9
29	33.8	33.9	33.6	33.5	33.7	31.1
30	25.5	25.4	24.7	24.8	24.7	26.7
*C*OMe		171.5			172.6	
CO*Me*		22.2			22.1	

in **1**. In the ^1H NMR spectrum, two coupled oxymethine signals were observed at δ 3.96 and 3.80, which could be assigned to H-15 and H-16, respectively. In the HMBC spectrum, correlations between the H-15 signal and the signals of C-8, C-14, and C-27 and between the H-16 signal and the signals of C-14, C-17, and C-18 were observed. The NOESY correlations of H-15 with H-26 and of H-16 with H-28 indicated α-configurations of the hydroxyl groups at C-15 and C-16. Thus, the structure of **3** was defined as 3-*O*-{α-L-rhamnopyranosyl-(1→2)-*β*-D-galactopyranosyl-(1→3)-[*β*-D-glucopyranosyl-(1→2)]-*β*-D-glucuronopyranosyl}-3*β*,15α,16α,28-tetrahydroxyolean-12-ene.

Ternstroemiaside D (**4**), the major saponin, was isolated as colorless crystals. It showed a $[M + K]^+$ ion peak at *m/z* 1321 and a $[M + Na]^+$ ion peak at *m/z* 1305 in the LRFABMS, which were consistent with a molecular formula of $C_{60}H_{98}O_{29}$. The ^1H and ^{13}C NMR spectra of **4** were similar to those of **3**. Methanolysis of **3** and **4** afforded the same aglycon (**3a**), and acid hydrolysis of **3** and **4** afforded the same sugar constituents. The HMQC spectrum of **4** showed additional anomeric peaks at δ 4.10 (d, $J = 7.5$ Hz) and δ_C 104.8 besides the peaks of the same tetrasaccharide unit as that of ternstroemiaside A (**1**). The additional sugar unit could be assigned as glucose (glc II) with the aid of 1D and 2D NMR experiments.[12] The HMBC correlation of C-28 (δ 78.1) with H-1 of glc II (δ 4.10) and ROESY correlations of H-28 (δ 3.47, 3.33) with H-1 of glc II (δ 4.10) indicated that this glucose unit was connected to C-28 of the aglycon. The cross-peaks between H-15, H-16, and H-1 of glc II were also observed in the ROESY experiment. The coupling constant of the anomeric proton ($J = 7.5$ Hz) and the ROESY correlations of H-1 with H-3 and H-5 of glc II indicated a *β*-configuration. Thus, the structure of **4** was elucidated as 3-*O*-{α-L-rhamnopyranosyl-(1→2)-*β*-D-galactopyranosyl-(1→3)-[*β*-D-glucopyranosyl-(1→2)]-*β*-D-glucuronopyranosyl}-28-*O*-*β*-D-glucopyranosyl-3*β*,15α,16α,28-tetrahydroxyolean-12-ene.

Ternstroemiaside E (**5**) was obtained as colorless crystals. The FABMS showed a $[M + K]^+$ ion peak at *m/z* 1347 and a $[M + Na]^+$ ion peak at *m/z* 1331, which indicated a molecular formula of $C_{62}H_{100}O_{29}$. Comparison of its NMR data and acid hydrolysis indicated the presence of the identical sugar moieties as those of **4**. In addition to the sugar moiety, the proton signal at δ 2.09 and the carbon signal at δ 172.6 indicated the presence of an acetyl group. The proton signal at δ 5.36, which correlated with C-15, C-18, and C-28 in the HMBC experiment, could be assigned to H-16. The downfield shift of H-16 and the HMBC correlation between H-16 and the carbonyl carbon of the acetyl group indicated the location of the acetyl group at C-16. The correlation between H-16 and H-28 in the NOESY spectrum suggested an α-configuration of the acetoxyl group at C-16. Therefore, the structure of **5** was established as 3-*O*-{α-L-rhamnopyranosyl-(1→2)-*β*-D-galactopyranosyl-(1→3)-[*β*-D-glucopyranosyl-(1→2)]-*β*-D-glucuronopyranosyl}-28-*O*-*β*-D-glucopyranosyl-16-*O*-acetylprimulagenin A.

Ternstroemiaside F (**6**) was isolated as colorless crystals. It showed a $[M + K]^+$ ion peak at *m/z* 1437 and a $[M + Na]^+$ ion peak at *m/z* 1421 in the FABMS, which indicated a molecular formula of $C_{65}H_{106}O_{32}$. Methanolysis of **6** afforded primulagenin A (**6a**)[3b] as an aglycon, which was identified by co-TLC with an authentic sample. Glycosidation shifts of C-3 (δ 92.3) and C-28 (δ 78.9) of the aglycon were observed, indicating **6** to be a 3,28-bisdesmoside. The HSQC spectrum showed anomeric peaks at δ 4.21/δ_C 103.4 and δ 4.48/δ_C 106.3 along with the anomeric peaks of the tetrasaccharide as observed in ternstroemiaside A (**1**). Comparison of the NMR data with those reported indicated the presence of additional glucose (glc II) and xylose (xyl) units.[12,13] The correlation between the oxymethylene carbon (δ 67.3) and the anomeric proton (δ 4.48) in the HMBC spectrum indicated that the xylose unit was in a pyranose form. The glycosidic linkages were determined according to the HMBC correlations between H-1 (δ 4.21) of glc II and C-28 (δ 78.9) and between H-1 (δ 4.48) of xyl and C-2 of glc II (δ 83.2). NOESY correlations between H-28 of the aglycon (δ 3.14, 3.64) and H-1 of glc II (δ 4.21) and between H-2 of glc II (δ 3.37) and H-1 of xyl (δ 4.48) were also observed. The coupling constants of the anomeric protons (7.5 Hz for glc II, 8.0 Hz for xyl) indicated *β*-configurations of these sugars. The stereochemistry of xylose was determined as the D-configuration by GLC analysis of its thiazolidine derivative.[8] Therefore, the structure of **6** was established as 3-*O*-{α-L-rhamnopyranosyl-(1→2)-*β*-D-galactopyranosyl-(1→3)-[*β*-D-glucopyranosyl-(1→2)]-*β*-D-glucuronopyranosyl}-28-*O*-[*β*-D-xylopyranosyl-(1→2)-*β*-D-glucopyranosyl]primulagenin A.

The known compound **7** was identified as 3-*O*-{α-L-rhamnopyranosyl-(1→2)-*β*-D-galactopyranosyl-(1→3)-[*β*-D-glucopyranosyl-(1→2)]-*β*-D-glucuronopyranosyl}-primulagenin A, which was isolated previously from *Rapanea melanophloeos*[14] and has been reported as a prosapogenol of sakuraso-saponin from *Primula sieboldi*.[15,16] A second known compound (**8**, desacyl-boninsaponin A) was isolated previously from *Schima mertensiana*.[16,17]

Experimental Section

General Experimental Procedures. Melting points were determined on a Fisher micro-melting point apparatus (hot-stage type) and are uncorrected. Optical rotations were measured using a JASCO DIP-370 digital polarimeter. The IR spectra were recorded on a JASCO FT-IR-410 spectropho-

Table 3. ^{1}H and ^{13}C NMR Data of the Sugar Moieties of Compounds **1**−**6** (CD_3OD)[a]

	1−**3**		**4**, **5**		**6**	
position	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
3-glcA						
1	4.52 (d, 7.5)	105.9	4.52 (d, 7.5)	105.8	4.52 (d, 8.0)	105.8
2	3.95 (t, 9.0)	79.1	3.95[b]	78.9	3.95 (t, 8.0)	78.9
3	4.05 (t, 9.0)	81.1	4.05 (t, 9.0)	80.9	4.05 (t, 9.0)	81.0
4	3.64 (t, 9.5)	71.7	3.63 (t, 9.0)	71.5	3.64[b]	71.6
5	3.88 (d, 11.0)	76.4	3.85 (dd, 11.0, 1.5)	76.2	3.87 (d, 11.5)	76.5
6		172.3		172.0		172.0
glc						
1	4.87 (d, 7.0)	102.6	4.87 (d, 7.5)	102.5	4.86[b]	102.6
2	3.23 (dd, 9.7, 7.5)	76.1	3.25 (dd, 9.5, 8.5)	76.0	3.23 (dd, 9.5, 7.5)	76.0
3	3.35 (t, 9.0)	78.2	3.35 (t, 9.0)	77.8	3.36[b]	77.8
4	3.08 (t, 9.5)	72.6	3.07 (t, 9.5)	72.5	3.06 (t, 9.5)	72.5
5	3.43 (t, 9.5)	78.0	3.40 (dt, 10.0, 2.0)	78.0	3.42[b]	77.9
6	3.88 (dd, 11.5, 1.5)	63.6	3.87 (d, 12.0)	63.6	3.86[b]	63.6
	3.55 (t, 13.0)		3.55 (t, 12.0)		3.53[b]	
gal						
1	5.17 (d, 7.5)	100.9	5.16 (d, 8.0)	100.9	5.17 (d, 7.5)	100.9
2	3.79 (t, 8.0)	76.0	3.79 (t, 8.0)	75.8	3.74[b]	75.8
3	3.73 (dd, 9.5, 3.0)	76.0	3.73 (dd, 9.0, 2.0)	75.8	3.73[b]	75.9
4	3.74 (br s)	71.7	3.74 (br s)	71.5	3.74[b]	71.6
5	3.54 (m)	77.0	3.53 (dd, 8.0, 4.0)	77.0	3.53[b]	77.0
6	3.81 (dd, 11.5, 7.5)	62.8	3.81 (dd, 11.5, 8.5)	62.8	3.80 (dd, 10.5, 8.5)	62.8
	3.66 (dd, 12.0, 3.5)		3.65 (dd, 12.0, 4.0)		3.65[b]	
rha						
1	5.28 (br s)	102.2	5.28 (d, 1.5)	102.0	5.28[b]	102.1
2	3.97 (br s)	72.6	3.95[b]	72.5	3.95[b]	72.5
3	3.71 (dd, 9.5, 3.0)	72.3	3.71 (dd, 10.0, 3.5)	72.2	3.68 (dd, 9.5, 3.0)	72.3
4	3.43 (t, 9.5)	73.8	3.42 (t, 9.5)	73.6	3.42 (t, 9.5)	73.7
5	4.10 (qd, 9.5, 6.0)	70.3	4.10 (m)	70.2	4.10 (qd, 9.5, 6.0)	70.2
6	1.28 (d, 6.0)	17.9	1.28 (d, 6.0)	17.8	1.28 (d, 6.5)	17.8
28-glc						
1			4.10 (d, 7.5)	104.8	4.21 (d, 7.5)	103.4
2			3.18 (dd, 9.0, 7.5)	74.9	3.37 (dd, 9.5, 7.5)	83.2
3			3.19 (t, 9.0)	77.8	3.53 (t, 9.0)	78.2
4			3.29 (t, 9.5)	71.5	3.30[b]	71.4
5			3.24 (m)	78.1	3.23 (t, 7.5)	77.9
6			3.85 (dd, 11.0, 1.5)	62.7	3.85 (d, 13.5)	62.6
			3.66 (t, 12.0)		3.66[b]	
xyl						
1					4.48 (d, 8.0)	106.3
2					3.20 (dd, 9.0, 7.5)	76.0
3					3.29[b]	77.7
4					3.50 (m)	71.0
5					3.84[b]	67.3
					3.16 (d, 11.0)	

[a] The chemical shifts are reported at 500 MHz for ^{1}H and at 50 MHz for ^{13}C; multiplicities and coupling constants of ^{1}H NMR data are in parentheses. [b] Overlapped with other signals.

tometer. NMR spectra were recorded on Bruker AC200 (^{13}C NMR) and Varian Inova 500 (^{1}H, DEPT, and 2D NMR spectra) instruments. TMS was used as an internal standard. LR-FABMS spectra were acquired on a JEOL JMS-SX-102A spectrometer. HRESIMS data were obtained on a Mariner spectrometer. Column chromatography was carried out over Kieselgel 60 (Merck, 63−200 μm). TLC was carried out over Kieselgel 60 F_{254} (Merck). HPLC was performed using a YMC ODS-H80 (250 × 10 mm, 4 μm, 80 Å) column with a Shodex RI detector. GLC was performed on a Hewlett-Packard HP6890 with a HP-1 column. The standard aglycons were obtained from the Graduate School of Pharmaceutical Sciences, Osaka University, Japan.

Plant Material. The fruits of *Ternstroemia japonica* were collected in October 1999 in Busan, Korea. The specimen was identified by K.S.I. A voucher specimen was deposited in the Natural Product Laboratory, Pusan National University, Busan, Korea.

Extraction and Isolation. Fresh fruits (3.5 kg) of *T. japonica* were extracted with MeOH three times at room temperature. The MeOH extract (50 g) was partitioned between EtOAc and H_2O. The H_2O layer was then extracted with *n*-BuOH. The *n*-BuOH extract was dissolved in MeOH and added dropwise into EtOAc to afford a precipitate of the crude saponin. The precipitate (6.0 g) was chromatographed over silica gel eluting with CH_2Cl_2−MeOH−H_2O (7:3:1, lower phase) to give six fractions. Fraction 4 (560 mg) was separated by reversed-phase HPLC (MeOH−H_2O, 95:30, 0.05% TFA) to give **1** (21.2 mg), **2** (42.2 mg), **3** (27.1 mg), **7** (74.7 mg), and **8** (23.2 mg). Fraction 6 (790 mg) was separated by reversed-phase HPLC (MeOH−H_2O, 70:30, 0.05% TFA) to give **4** (150.8 mg), **5** (9.4 mg), and **6** (32.4 mg).

Ternstroemiaside A (1): colorless needles; mp 239−242 °C; $[\alpha]^{20}_D$ −29.3° (*c* 0.3, MeOH); IR (KBr disk) ν_{max} 3390 (OH), 1734 (COOH) cm^{-1}; ^{1}H NMR data, see Tables 1 and 3; ^{13}C NMR data, see Tables 2 and 3; LRFABMS *m*/*z* 1159 $[M + K]^+$, 1143 $[M + Na]^+$; HRESIMS *m*/*z* 1121.5703 $[M + H]^+$ (calcd for $C_{54}H_{89}O_{24}$, 1121.5738)

Ternstroemiaside B (2): colorless needles; mp 225−230 °C; $[\alpha]^{20}_D$ −30.9° (*c* 0.5, MeOH); IR (KBr disk) ν_{max} 3390 (OH), 1715 (ester) cm^{-1}; ^{1}H NMR data, see Tables 1 and 3; ^{13}C NMR data, see Tables 2 and 3; FABMS *m*/*z* 1201 $[M + K]^+$, 1185 $[M + Na]^+$; HRESIMS *m*/*z* 1163.5842 $[M + H]^+$ (calcd for $C_{56}H_{91}O_{25}$, 1163.5844).

Ternstroemiaside C (3): colorless needles; mp 230−237 °C; $[\alpha]^{20}_D$ −18.3° (*c* 0.5, MeOH); IR (KBr disk) ν_{max} 3390 (OH), 1734 (COOH) cm^{-1}; ^{1}H NMR data, see Tables 1 and 3; ^{13}C NMR data, see Tables 2 and 3; FABMS *m*/*z* 1159 $[M + K]^+$,

1143 $[M + Na]^+$; HRESIMS *m/z* 1121.5753 $[M + H]^+$ (calcd for $C_{54}H_{89}O_{24}$, 1121.5738).

Ternstroemiaside D (4): colorless crystals; mp 231 °C; $[\alpha]^{20}_D$ −32.1° (*c* 1.3, MeOH); IR (KBr disk) ν_{max} 3400 (OH), 1657 (COOH) cm^{-1}; ^1H NMR data, see Tables 1 and 3; ^{13}C NMR data, see Tables 2 and 3; FABMS *m/z* 1321 $[M + K]^+$, 1305 $[M + Na]^+$; HRESIMS *m/z* 661.2952 $[M + H + K]^{2+}$ (calcd for $C_{60}H_{99}O_{29}K$, 1322.5898).

Ternstroemiaside E (5): colorless crystals; mp 228−230 °C; $[\alpha]^{20}_D$ −38.2° (*c* 1.6, MeOH); IR (KBr disk) ν_{max} 3390 (OH), 1715 (ester) cm^{-1}; ^1H NMR data, see Tables 1 and 3; ^{13}C NMR data, see Tables 2 and 3; FABMS, *m/z* 1347 $[M + K]^+$, 1331 $[M + Na]^+$; HRESIMS *m/z* 674.3003 $[M + H + K]^{2+}$ (calcd for $C_{62}H_{101}O_{29}K$, 1348.6055).

Ternstroemiaside F (6): colorless crystals; mp 216−222 °C; $[\alpha]^{20}_D$ −39.0° (*c* 0.5, MeOH); IR (KBr disk) ν_{max} 3400 (OH), 1657 (COOH) cm^{-1}; ^1H NMR data, see Tables 1 and 3; ^{13}C NMR data, see Tables 2 and 3; FABMS *m/z* 1437 $[M + K]^+$, 1421 $[M + Na]^+$.

Acid Hydrolysis of Saponins. Each saponin (**1**−**6**, 2 mg) was refluxed with 7% HCl (1 mL) for 3 h. The reaction mixture was partitioned between EtOAc and H_2O. The H_2O layer was concentrated and analyzed by co-TLC (Si gel) with the authentic sugars (CH_2Cl_2−MeOH−H_2O, 6.5:4.0:0.8; R_f, 0.13 for glcA, 0.47 for gal, 0.53 for glc, 0.52 for xyl, and 0.78 for rha). The identity of each sugar was further confirmed by comparison of the retention time with those of standard samples using HPLC: t_R (min) glc (5.75), gal (6.1), xyl (4.25), and rha (3.73). HPLC analysis was performed with a Supelcosil LC-NH_2 column (250 × 4.6 mm, 5 μm) eluting with CH_3CN−H_2O (75:25) at a flow rate of 1.5 mL/min.

Methanolysis of Saponins. Each saponin (**1**−**6**, 8 mg) was refluxed with 9% HCl−MeOH (2 mL) for 1 h, neutralized with Ag_2CO_3, and filtered to remove the precipitate (AgCl). Evaporation of the filtrate under reduced pressure afforded a product that was subjected to HPLC (MeOH−H_2O, 10:1) to give respective aglycons. The aglycons were identified as camelliagenin A (**1a**), primulagenin A (**6a**), and A_1-barrigenol (**8a**) by co-TLC with authentic samples.

Stereochemistry of the Sugars. Compounds **1** and **6** (5 mg each) were separately refluxed in 5% aqueous H_2SO_4−1,4-dioxane (1:1, 2 mL) for 1 h. Each reaction mixture was passed through Dowex SBR ($^-$OH form), and the filtrate was condensed. The resulting residues were passed through a Sep-Pack C_{18} cartridge eluting with H_2O. The filtrate was condensed and heated in l-cysteine methyl hydrochloride (5 mg) and pyridine (0.5 mg) for 1 h at 60 °C. The reaction mixture was heated with *N,O*-bis(trimethylsilyl)trifluoroacetamide (0.3 mg) for another 1 h at 60 °C, with the supernatants of the reaction mixtures employed for GLC analysis. Identification of the thiazolidine derivatives of D-glucose, D-galactose, D-glucuronic acid, D-xylose, and L-rhamnose was carried out by comparison of their retention times with those of standard samples: t_R (min) d-glucose (10.46), D-galactose (10.78), D-glucuronic acid (10.93), D-xylose (7.38), and L-rhamnose (8.43). GLC analysis was performed with an HP-1 column (30 m, 0.32 mm, 0.25 μm) with an initial temperature of 200 °C for 3 min and then temperature programming to 250 °C at a rate of 5 °C/min.

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