Three Unusual 22-β-*O*-23-Hydroxy-(5α)-spirostanol Glycosides from the Fruits of *Solanum torvum*

Yoshihiko IIDA,[a] Yoshihiro YANAI,[a] Masateru ONO,[b] Tsuyoshi IKEDA,[a] and Toshihiro NOHARA*,[a]

[a] *Faculty of Medical and Pharmaceutical Sciences, Kumamoto University; 5–1 Oe-honmachi, Kumamoto 862–0973, Japan: and* [b] *School of Agriculture, Kyushu Tokai University; 5435 Choyo, Aso, Kumamoto 869–1404, Japan.*
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Three novel 22-β-*O*-spirostanol oligoglycosides, torvosides J (1), K (2) and L (3) have been isolated from the fruits of *Solanum torvum* SWARTZ and their chemical structures have been characterized based on the spectroscopic means. They are worth of note as rare 22-β-*O*-spirostanol glycosides.

Key words *Solanum torvum*; steroid glycoside; 22-β-*O*-spirostanol; Thai cuisine

Solanum torvum SWARTZ (Solanaceae) is a small shrub, of which fruits are commonly available in the markets and are used as a vegetable regarded as an essential ingredient in Thai cuisine. Previously, we reported seven steroidal glycosides from the aerial parts and the roots of this plant.[1)] As regard with the former reports of the constituents in this plant, neochlorogenin,[2,3)] chlorogenin,[3,4)] paniculogenin,[2,5)] solaspigenin,[5,6)] neosolaspigenin,[5,6)] and torvonin-B[7)] were known. Recently, an additional steroidal glycoside, torvoside H[8)] was reported. In this time, three unusual 22-β-*O*-spirostanol glycosides have been isolated from the fruits of this plant.

The methanolic extract (33.4 g) of fresh fruits (600 g) of *Solanum torvum* was subjected to high-porous polystyrene gel (Diaion) to elute gradually with H_2O→50% MeOH→MeOH→acetone. The MeOH eluate was subsequently separated by using silica gel chromatography and HPLC to afford torvoside J (**1**, 5.4 mg), torvoside K (**2**, 8.3 mg), and torvoside L (**3**, 4.2 mg) together with known steroidal glycosides, torvosides A[1)] (2.54 g) and H[8)] (29.2 mg).

Torvoside J (**1**), obtained as an amorphous powder, $[\alpha]_D$ +53.1° (MeOH) showed a quasimolecular ion peak at *m/z* 763 due to $[M+Na]^+$ in the positive FAB-MS. The ^{1}H-NMR signals (in pyridine-d_5) of **1** displayed two tertiary methyl groups at δ 0.85 (6H, s), two secondary methyl groups at δ 0.73 (3H, d, J=6.7 Hz), 1.53 (3H, d, J=6.7 Hz), two protons of oxygen-bearing methylene group at δ 3.63, 3.71 (2H, overlapped), a proton of oxygen-bearing methine group at δ 4.04 (1H, br s), and two anomerics at δ 4.76 (1H, d, J=9.2 Hz) and 6.29 (1H, s). The ^{13}C-NMR spectrum (in pyridine-d_5) showed totals 39 carbon signals, 12 carbon signals among which were assignable to α-L-rhamnopyranosyl-(1→3)-β-D-quinovopyranosyl moiety by comparing with those of already reported sugar residue[1)] as listed in Table 1. The absolute configurations of the respective sugars were determined by using HPLC equipped optical rotatory instrument after acid hydrolysis of **1**. The remaining 27 carbons originating from the sapogenol moiety were constituted of eight methylene carbons at δ 21.1, 32.3, 32.5, 33.2, 37.8, 37.9, 39.9, 41.4, seven methine carbons at δ 24.6, 34.4, 41.4, 51.4, 54.0, 56.5, 64.9, two quaternary carbons at δ 36.8, 41.2, four methyl carbons at δ 13.6, 16.5, 17.3, 17.4, four oxygen-bearing methine carbons at δ 70.3, 70.7, 79.5, 81.5, one oxygen-bearing methylene carbon at δ 67.0, and one acetal carbon at δ 109.6. To reveal the connectivities of the respective protons and carbons, the ^{1}H-detected heteronuclear multiple-bond correlation (HMBC) spectrum was examined and long-range correlations were observed from H_3-19 to C-1/C-10/C-5/C-9, H_3-18 to C-12/C-13/C-14/C-17, H_3-21 to C-17/C-20/C-22, H_3-27 to C-24/C-25/C-26, H-25 to C-23/C-26, and from H_2-26 to C-22, as shown in Fig. 1. Especially, the HMBC between H-25 (δ 2.47) and C-23 (δ 70.3) indicated the presence of a hydroxyl group at C-23. The proton signal at C-23 appeared as a broad singlet at δ 4.07, suggesting it to be *equatorial*. Moreover, the HMBCs between H_3-19 and C-5, between H-5 and C-3, and between H-5 and C-6 revealed the occurrence of the hydroxyl group at C-3 and C-6.

Since signals due to H-3 and H-6 were overlapped to other sugar signals, their coupling constants could not be discriminated. However, the ^{13}C-NMR signals due to C-3, C-6 and their surrounding carbons at C-2, C-4, C-5, and C-7 were coincident with those of **1**,[1)] so that the configuration at C-3 and C-6 were conceivable to be identical with those of **1**. Usually, the configuration at C-25 is determined by the signal pattern of H_2-26. However, the signals due to H_2-26 appeared around at δ 3.70, which were overlapped with the other signals of H-3 and H-6 in the sapogenol and of the quinovosyl H-4 and H-5, so that they could not be discriminated. When the methyl group at C-25 is *axial*, it would show a remarkable lower shift due to 1,3-diaxial correlation with the hydroxyl group at C-23. But, the signal due to H_3-27 practically appeared at δ 0.73, suggesting it to be equatorial. Next, as for the configuration at C-22, the H_3-21 signals in other C-23-hydroxyl spirostanol derivatives were referred. The H_3-21 appeared at

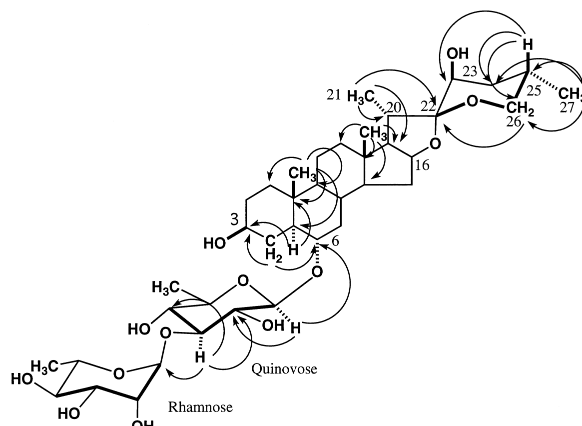


Fig. 1. Key HMBC of Torvoside J (**1**)

* To whom correspondence should be addressed. e-mail: none@gpo.kumamoto-u.ac.jp © 2005 Pharmaceutical Society of Japan

Table 1. ^{1}H- and ^{13}C-NMR Spectra Data for Torvosides J (**1**), K (**2**) and L (**3**) (in Pyridine-d_5)

Position	Torvoside J (**1**)		Torvoside K (**2**)		Torvoside L (**3**)	
	δ_C	δ_H (m, J in Hz)	δ_C	δ_H (m, J in Hz)	δ_C	δ_H (m, J in Hz)
1	37.8	0.96 (ddd, 2.5, 12.8, 14.0), 1.66*	37.8	0.94 (ddd, 3.7, 14.0, 14.0), 1.64*	37.8	0.91 (ddd, 3.7, 12.8, 13.4), 1.64*
2	32.3	1.74*, 2.02*	32.3	1.68*, 2.03 (br d, 12.8)	32.3	1.62*, 2.02*
3	70.7	3.74*	70.7	3.74*	70.7	3.69*
4	33.2	1.64*, 3.17 (br d, 11.0)	33.2	1.61*, 3.17 (br d, 11.0)	33.2	1.61*, 3.56 (br d, 12.2)
5	51.4	1.32 (ddd, 3.1, 12.2, 13.5)	51.4	1.32 (ddd, 2.4, 7.3, 13.4)	51.4	1.29*
6	79.5	3.67*	79.5	3.65*	79.4	3.65*
7	41.1	1.21*, 2.53 (dt, 3.7, 12.2)	41.4	1.23*, 2.53 (dt, 4.3, 12.8)	41.5	1.17*, 2.53 (dt, 3.7, 12.8)
8	34.4	1.69*	34.3	1.66*	34.2	1.68*
9	54.0	0.60 (ddd, 4.8, 11.3, 11,6)	54.0	0.60 (ddd, 3.7, 11.3, 11.6)	54.1	0.59 (ddd, 3.6, 11.0, 11.3)
10	36.8		36.8		36.8	
11	21.1	1.23*, 1.46*	21.3	1.20*, 1.43*	21.3	1.26*, 1.46*
12	39.9	1.05*, 1.74*	40.0	1.06*, 1.71*	40.4	1.09*, 1.74*
13	41.2		41.2		41.5	
14	56.5	1.08*	56.5	1.09*	55.9	1.06*
15	32.5	1.49*, 2.11*	32.4	1.45*, 2.09*	34.2	1.51*, 2.12*
16	81.5	4.67 (ddd, 6.1, 7.9, 7.9)	81.6	4.64*	84.4	5.18 (ddd, 6.7, 6.7, 8.6)
17	64.9	1.81 (dd, 5.5, 7.9)	64.6	1.82*	63.8	2.04*
18	16.5	0.85, s	16.6	0.83, s	16.7	1.02, s
19	13.6	0.85, s	13.6	0.84, s	13.6	0.84, s
20	41.4	2.60 (dt, 6.7, 7.3)	40.9	2.64 (dt, 6.7, 12.8)	43.1	2.60 (dt, 6.7, 7.3)
21	17.3	1.53 (d, 6.7)	17.2	1.55 (d, 6.7)	17.1	1.53 (d, 7.3)
22	109.6		110.5		113.0	
23	70.3	4.04, br s	70.2	4.06, br s	70.4	4.06 (dd, 4.3, 11.0)
24	37.9	1.92 (ddd, 2.3, 12.8, 13.4), 1.97, m	34.6	1.80*, 2.35 (dt, 4.9, 13.4)	38.7	1.93 (dt, 11.6, 12.2), 2.05, m
25	24.6	2.47, m	27.3	1.73, m	31.2	1.82, m
26	67.0	3.63*, 3.71*	65.4	3.55 (d, 11.0), 4.20 (dd, 3.7, 11.0)	70.7	3.67*, 3.75*
27	17.4	0.73 (d, 6.7)	20.5	1.53 (d, 7.3)	16.5	0.73 (d, 6.1)
Inner qui-1	105.6	4.76 (d, 9.2)	105.6	4.76 (d, 7.9)	105.5	4.78 (d, 7.9)
2	76.2	4.03 (t, 8.6)	76.2	4.03 (t, 8.4)	76.2	4.03 (t, 8.6)
3	83.7	4.26 (t, 9.2)	83.7	4.27 (t, 9.2)	83.7	4.27 (t, 9.2)
4	75.3	3.61*	75.3	3.63*	75.3	3.61*
5	72.8	3.72*	72.6	3.72*	72.6	3.71*
6	18.8	1.63 (d, 6.1)	18.8	1.63 (d, 6.1)	18.8	1.63 (d, 6.1)
Term. rha-1	103.1	6.29, s	103.1	6.30, s	103.1	6.30, s
2	72.7	4.82 (d, 2.4)	72.7	4.83 (dd, 1.2, 3.1)	72.7	4.83 (dd, 1.8, 3.7)
3	72.8	4.61 (dd, 3.7, 9.2)	72.8	4.61(dd, 3.7, 9.2)	72.8	4.60 (dd, 3.7, 9.2)
4	74.2	4.35 (t, 9.2)	74.2	4.35 (t, 9.8)	74.2	4.35 (t, 9.8)
5	70.0	5.01*	70.0	5.02*	70.0	5.02*
6	18.6	1.71 (d, 6.1)	18.6	1.72 (d, 6.1)	18.6	1.72 (d, 6.1)

* Overlapped signals.

δ 1.26 in 22-α-*O*-spirostanol glycoside, anguivoside III,[9] and it also occurred at δ 1.17 in paniculogenin.[6] The H_3-21 signal in torvoside J (**1**) showed a marked lower shift at δ 1.52. It would be rationalized that the hydroxyl group at C-23 approached to the H_3-21 in 22-β-*O*-configuation. The H_3-21 was regarded to be extremely influenced by the anisotropic effect of pyridine oriented to the hydroxyl at C-23. Consequently, torvoside J (**1**) was characterized as (22*R*,23*S*,25*S*)-3β,6α,23-trihydroxy-5α-spirostane. In almost cases of spirostanol derivatives, generally they take 22-α-*O*-configuration, therefore this example is very rare except for hispigenin,[9—11] which is interpreted in the section of torvoside L (**3**).

Meanwhile, as for sugar linkage, the HMBCs between the rhamnopyranosyl C-1 and the inner quinovopyranosyl H-3, and between the quinovopyranosyl H-1 and the sapogenol C-6 were observed as shown in Fig. 1. Additionally, the ^{1}H–^{1}H COSY showed sequential correlations for a series from H_2-1 to H-9, sequences of H_2-15-H-16-H-17-H-20-H_3-21, and H-23-H-24-H-25-H_3-27-H_2-26, the rhamnopyranosyl H_3-6-H-5-H-4-H-3-H-2 and the quinovopyranosyl H_3-6-H-5-H-4-H-3-H-2-H-1, which made the assignment of the respective proton and carbon signals. Consequently, the structure of torvoside J (**1**) was represented as 6-*O*-α-L-rhamnopyranosyl-(1→3)-β-D-quinovopyranosyl-(22*R*,23*S*,25*S*)-3β,6α,23-trihydroxy-5α-spirostane.

Torvoside K (**2**) was obtained as an amorphous powder showing $[\alpha]_D$ −59.3° (MeOH). A quasimolecular ion peak at *m/z* 763 due to $[M+Na]^+$ in the positive FAB-MS was also given. The ^{13}C-NMR spectrum displayed total 39 carbon signals, 12 ones among them were attributable to the α-L-rhamnopyranosyl-(1→3)-β-D-quinovopyranosyl, and the rest 27 carbon signals belonged to the sapogenol moiety, that is, it was composed of eight methylene carbons, seven methine carbons, two quaternary carbons, four methyl groups, four oxygen-bearing methine carbons, one oxygen-bearing methylene carbon and one ketal carbon. The carbon composition was identical with that of **1**. The above ^{13}C-NMR signals and the respective proton signals at δ 0.83 (3H, s), 0.84 (3H, s), 1.53 (3H, d, J=7.3 Hz), 1.55 (3H, d, J=6.7 Hz), 1.63, 1.71 (each 3H, d, J=6.1 Hz), 3.55 (1H, d, J=11.0 Hz), 4.20 (1H, dd, J=3.7, 11.0 Hz), 4.06 (1H, br s), 4.76 (1H, d, J=7.9 Hz),

6.30 (1H, s) were assigned by the ^{1}H–^{1}H shift correlated spectroscopy (COSY), ^{1}H-detected heteronuclear correlation through multiple quantum coherence (HMQC) and HMBC measurements as listed in Table 1. The configuration at C-25 was decided by the H_2-26 signals at δ 3.55 (1H, d, J=11.0 Hz) and 4.20 (1H, dd, J=3.7, 11.0 Hz) to be axial. Actually, the signals due to H_3-27 was considerably lower shifted to δ 1.53, also indicating the H_3-27 at C-25 to be axial to form a 1,3-diaxial connection with the hydroxyl group at C-23. The configuration at C-22 was estimated as R (22-β-O) because the signals of H_3-21 was also distinctly lower-shifted to δ 1.56 owing to the presence of the hydroxyl group at C-23. The HMBCs between the terminal rhamnopyranosyl C-1 and the inner quinovopyranosyl H-3, and between the quinovopyranosyl H-1 and the sapogenol C-6 disclosed the sugar linkage. Therefore, torvoside K (**2**) was determined to be 6-O-α-L-rhamnopyranosyl-(1→3)-β-D-quinovopyranosyl (22R,23S,25R)-3β,6α,23-trihydroxy-5α-spirostane.

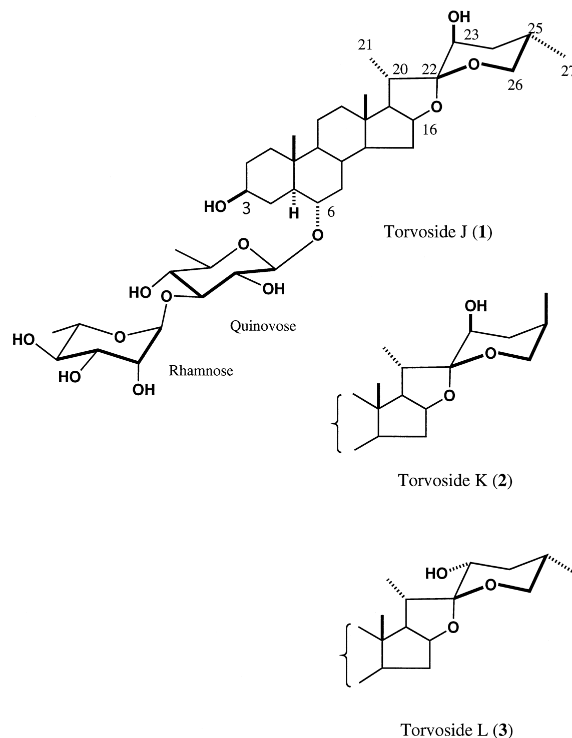
Previously, the structures of torvonin-B[7] and torvoside C,[1] were reported as glycosides of neosolaspigenin[5,6] having 22-α-O-spirostane skeleton because their ^{13}C-NMR signals due to the aglycone moiety were identical with those of neosolaspigenin. However, the ^{13}C-NMR signals of torvonin-B[7] and torvoside C[1] were coincident with those of the sapogenol moiety of this torvoside K (**2**). Moreover, the ^{1}H-NMR signals of neosolaspigenin were also identical with those of **2** except for glycosylation shift. The heptaacetate of **2** was superimposable upon those of neosolaspigenin triacetate ($CDCl_3$)[10,11] besides the signals with glycosylation shift. Moreover, all the ^{13}C-NMR signals including the sugar part of **2** were almost identical with those of torvonin-B, although the assignments were partially different from each other. Therefore, the structure of torvonin-B was conceivable to identical to torvoside K (**2**).

Consequently, the structures of neosolaspigenin, torvonin-B and torvoside C should be revised to the reversal configuration at C-22, namely 22-O-β-spirostanes as shown in Fig. 2.

Torvoside L (**3**) showed $[\alpha]_D$ −3.8° (MeOH) and a quasi-molecular ion peak at m/z 763 due to $[M+Na]^+$ in the positive FAB-MS, from which this compound was also regarded as an isomer of torvoside J (**1**) or K (**2**). By the aid of the ^{1}H–^{1}H COSY, HMQC and HMBC of torvoside L (**3**) as well as torvoside J (**1**) and torvoside K (**2**), the ^{1}H and ^{13}C-signals were assigned as listed in Table 1. The proton signal due to H-23 appeared at δ 4.06 (1H, dd, J=4.3, 11.0 Hz), being assignable to the axial one. The equatorial hydroxyl group at C-23 approached to the H-16, thus causing an extreme lower-shift of H-16 to δ 5.18 (1H, ddd, J=6.7, 6.7, 8.6 Hz). The H_2-26 signals appeared at δ 3.70 were overlapped with those of the quinovopyranosyl H-4 and H-5 and the sapogenol H-6, and its pattern was similar with those of torvoside J (**1**), suggesting the configuration at C-25 to be S (the methyl group at C-25: equatorial). The sugar linkage was also the same with those of **1** and **2**.

Furthermore, the sapogenol (**4**) of torvoside L (**3**) was separately prepared by a sequence of the reaction of sodium periodate, sodium borohydride and weak acid treatment of **3**. This sapogenol showed proton signals due to H_3-21 (d, J=6.1 Hz, at δ 1.52), H-16 (ddd, J=6.8, 6.8, 8.2 Hz at δ 5.22) and H-23 (dd, J=3.0, 10.1 Hz, at δ 4.05) in the ^{1}H-NMR spectrum and carbon signal due to C-20 at δ 43.0 in the ^{13}C-NMR spectrum, which indicated **4** to be a 22-O-β-spirostanol.

Therefore, the structure of torvoside L (**3**) was determined to be 6-O-α-L-rhamnopyranosyl-(1→3)-β-D-quinovopyranosyl (22R,23R,25S)-3β,6α,23-trihydroxy-5α-spirostane.



Hispigenin[9—11] was the first report for 22-β-O-spirostanol. When the ^{1}H- and ^{13}C-NMR spectra of **3** were compared with those of hispigenin, the both were approximately identical to each other expect for small differences due to different solvent measured and glycosylation shifts around at C-6. Characteristic signals assignable to H_3-21 (δ 1.47, d, J=7.0 Hz) and H-16 at δ 5.16 (1H, ddd, J=8.0, 8.0, 8.0 Hz) were appeared in hispigenin, in which the signal due to H-23 appeared at δ 5.90 (1H, d, J=7.0 Hz) is conceivable to be an error of τ value (real value is regarded as δ 4.10). The sapogenol of torvoside L (**3**) corresponds to hispigenin, of which C-23-OH should be corrected from axial to equatorial as shown in Fig. 2.

As a result, for the discrimination between 22-α-O- and 22-β-O- in case of 23-hydroxyspirostanol, the chemical shifts at C-20 in the ^{13}C-NMR (in pyridine-d_5) and at H_3-21 in the ^{1}H-NMR spectra (in pyridine-d_5) are effectively available, namely, 22-α-O-spirostanol: H_3-21 appeared at δ_H 1.07—1.26; C-20 appeared at δ_C 35.0—36.2, 22-β-O-spirostanol: H_3-21 appeared at δ_H 1.53—1.54; C-20 appeared at δ_C 43.1-44.1.

Experimental

Optical rotations were measured on a JASCO DIP-1000KUY (l=0.5) automatic digital polarimeter at 15 °C. TLC was performed on precoated silica gel 60 F_{254} plates (Merck). Column chromatographies were carried out on Kieselgel 60 (40—100 mesh and 230—400 mesh, Kanto Chem.), Diaion HP-20 (Mitsubishi Chemical Ind.). HPLC was conducted on an ODS column (Waters Cosmosil $5C_{18}$-MSII, ϕ20×250 mm, 5 μm) using a Hitachi L-

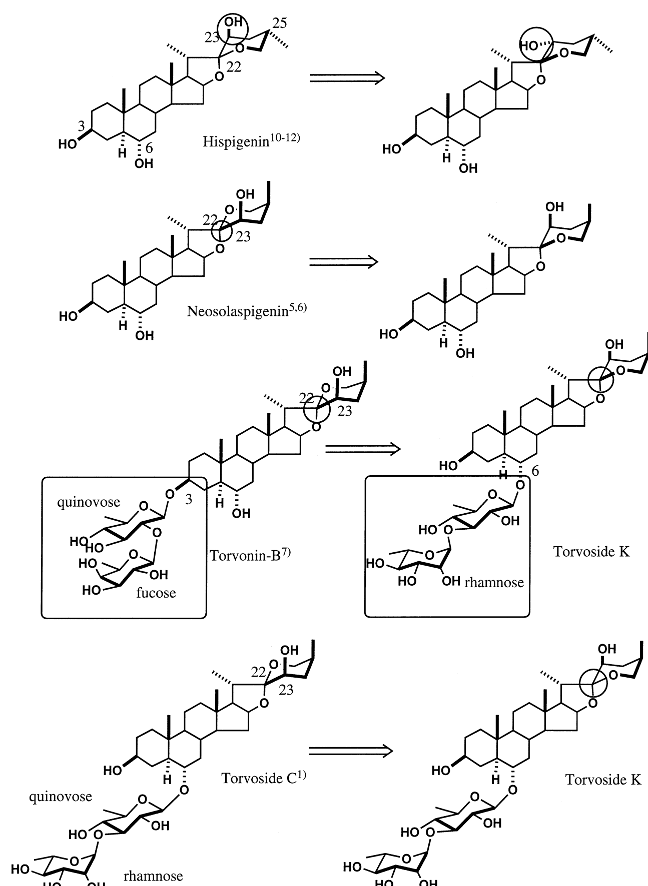


Fig. 2. Revision of Reported Structures

6000 pump equiped with a differential refractometer (JASCO 830-RI). The FAB-MS were measured with a JEOL JMS-DX303HF spectrometers (Xe atom beam, accel. voltage 2—3 kV, matrix glycerol), 200—300 mA, ioni. The NMR spectra were recorded at 500 MHz for ^{1}H and 125 MHz for ^{13}C on a JNC-A500 NMR spectrometer and chemical shifts were given on a δ (ppm) scale with tetramethylsilane as an internal standard. Standard pulse sequences were employed for the DEPT, HMQC and HMBC experiments. NOESY spectra were measured with mixing times of 600 ms. Sugars were analyzed by using HPLC with 80% acetonitrile (flow rate: 0.8 ml/min, column oven 30 °C) equipped with optical rotatory instrument (column oven: JASCO CO-2060, pump: Pu-2080, detection of specific rotation: OR-2090 for and column: YMC-Pac R&D Polyamine II).

Extraction and Isolation The fruits (600 g) purchased at market in Bangkok, Thailand were extracted with refluxing MeOH, which was evaporated under reduced pressure to give a MeOH extractive (33.4 g). The extractive was passed through Diaion HP-20 and successively eluted with water, 50% MeOH, MeOH and acetone. The MeOH eluate (6.95 g) was chromatographed on silica gel with $CHCl_3$: MeOH : water = 8 : 2 : 0.1, 7 : 3 : 0.2, 7 : 3 : 0.5, MeOH, gradient, to afford six fractions. Fraction 2 (157.6 mg) was further separated with silica gel ($CHCl_3$: MeOH : water system) and HPLC (50% MeOH) to provide torvosides J (**1**, 5.4 mg), K (**2**, 8.3 mg) and L (**3**, 4.2 mg) together with torvoside A (2535.8 mg) from fraction 5 and torvosides I (131.4 mg) and H (29.2 mg). Torvoside L (**3**, 98 mg) was separately prepared in the same manner from the fruits (2.43 kg) and used for the reaction obtaining the sapogenol.

Torvoside J (1) An amorphous powder, $[\alpha]_D$ −53.1° (c=0.4, MeOH), Positive FAB-MS (m/z): 763 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR spectra (in pyridine-d_5) δ: Table 1. *Anal.* Calcd for $C_{39}H_{64}O_{13}$: C, 63.22; H, 8.71. Found: C, 63.24; H, 8.72.

A small amount of **1** (2.1 mg) was refluxed with 1 N HCl–MeOH for 1 h, concentrated, added with water and heated for 30 min on the hot bath. The resultant was passed through Amberlite IR-400A to give sugar solution, which was subjected HPLC equipped with optical rotatory instrument. L-Rhamnose: t_R 7.6 min, negative peak; D-qui: t_R 19.0 min, positive peak (standard, L-rha t_R: 7.8 min negative peak; D-qui: t_R 19.5 min, positive peak; D-glu, t_R 38.2 min, positive peak).

Torvoside K (2) An amorphous powder, $[\alpha]_D$ −59.3° (c=0.4, MeOH), Positive FAB-MS (m/z): 763 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR spectra (in pyridine-d_5) δ: Table 1. *Anal.* Calcd for $C_{39}H_{64}O_{13}$: C, 63.22; H, 8.71. Found: C, 63.20; H, 8.73.

Torvoside K Heptaacetate A mixture of torvoside K (**2**, 10.8 mg), pyridine (1 ml) and acetic anhydride (1 ml) was left stand at r.t. for one night. Usual work-up gave an acetate (8 mg). An amorphous powder, ^{1}H-NMR (in $CDCl_3$) δ: 0.75 (3H, s, H_3-19), 0.84 (3H, s, H_3-18), 1.98 (3H, d, J=7.3 Hz, H_3-21), 1.14 (3H, d, J=6.1 Hz, qui H_3-6), 1.18 (3H, d, J=6.1 Hz, rha H_3-6), 1.19 (3H, d, J=7.3 Hz, H_3-27), 3.23 (1H, ddd, J=4.3, 10.4, 11.6 Hz, H-6), 3.38 (1H, m, qui H-5), 3.40 (1H, br d, J=11.0 Hz, H-26 *ax.*), 3.70 (1H, dd, J=9.2, 10.4 Hz, qui H-3), 3.88 (1H, m, rha H-5), 4.02 (1H, dd, J=3.5, 11.0 Hz, H-26 eq.), 4.36 (1H, d, J=7.9 Hz, qui H-1), 4.49 (1H, m, H-16), 4.64 (1H, m, H-3), 4.77 (1H, br s, H-23), 4.78 (1H, br s, rha H-1), 4.82 (1H, dd, J=9.2, 9.8 Hz, qui H-4), 4.98 (1H, overlapped, H-2), 5.00 (1H, overlapped, rha H-4), 5.06 (1H, overlapped, rha H-3), 5.07 (1H, overlapped, rha H-2). ^{13}C-NMR (in $CDCl_3$) δ: C-1-27: 36.9, 27.2, 73.3, 31.8, 49.7, 80.5, 40.0, 34.1, 53.4, 36.5, 20.8, 39.4, 41.0, 56.1, 28.3, 81.6, 63.9, 16.2, 13.4, 40.7, 15.9, 107.7, 71.9, 30.8, 25.9, 64.8, 19.3, inner qui C-1-6: 102.2, 72.5, 81.8, 74.6, 69.0, 17.2, term. Rha C-1-6: 99.5, 70.0, 70.1, 70.8, 67.5, 17.5.

Torvoside L (3) An amorphous powder, showed $[\alpha]_D$ −3.8° (c=0.4, MeOH). Positive FAB-MS (m/z): 763 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR spectra (in pyridine-d_5) δ: Table 1. *Anal.* Calcd for $C_{39}H_{64}O_{13}$: C, 63.22; H, 8.71. Found: C, 63.19; H, 8.68.

Sapogenol (4) of Tornoside L (3) To a solution of torvoside L (**3**, 98 mg) in EtOH and water (each 5 ml), sodium periodate (200 mg) was added and stirred at r.t. for 30 min. After removal of the solution under reduced pressure, the residue was subjected to Diaion column chromatography to give the product, which was then dissolved in MeOH (4 ml) and reduced with sodium borohydride (177 mg). The resultant was concentrated and passed through Diaion column to give the MeOH eluate, which was treated with 0.5 N HCl–MeOH (2 ml) and chromatographed on silica gel with $CHCl_3$–MeOH=20 : 1 to give the sapogenol (**4**, 32 mg) as an amorphous powder, showed $[\alpha]_D$ −10.8° (c=0.4, MeOH). ^{1}H-NMR (pyridine-d_5) δ: 0.72 (3H, d, J=6.1 Hz, H_3-27), 0.87 (3H, s, H_3-19), 1.05 (3H, s, H_3-18), 1.52 (3H, d, J=7.3 Hz, H_3-21), 3.64 (2H, m, H_2-26), 3.89 (2H, m, H-3, 6), 4.05 (1H, dd, J=3.0, 10.1 Hz, H-23), 5.22 (1H, ddd, J=6.7, 6.8, 8.2 Hz). ^{13}C-NMR (pyridine-d_5) δ: C-1-27, 38.6, 32.4, 71.0, 33.7, 52.8, 70.3, 43.0, 34.3, 55.9, 36.6, 21.4, 40.4, 41.5, 54.5, 34.3, 84.3, 63.7, 16.6, 13.8, 43.0, 16.8, 112.9, 68.6, 38.0, 32.4, 68.8, 17.1.

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