Saponins from *Talinum triangulare*

Hiroshi KOHDA,*,[a] Yasutoshi YAMAOKA,[a] Syuji MORINAGA,[a] Muh ISHAK,[b] and Muchsin DARISE[b]

Institute of Pharmaceutical Sciences, School of Medicine, Hiroshima University,[a] 1–2–3, Kasumi, Minami-ku, Hiroshima 734, Japan and Department of Pharmacy, Faculty of Mathematics and Natural Sciences, Hasanuddin University,[b] Jalan Perintis Kemerdekaan, Ujung Pandang South Sulawesi, Indonesia. *Received January 28, 1992*

***Talinum triangulare* WILLD. have been used as a traditional treatment for tonic in Indonesia. From roots of this plant, two saponins were isolated. One was identified as chikusetsusaponin IVa, a known saponin of oleanolic acid from rhizomes of *Panax* spp. The other was a new saponin, and was elucidated as β-D-glucopyranosyl methyl spergulagenate 3-*O*-β-D-glucuronopyranoside.**

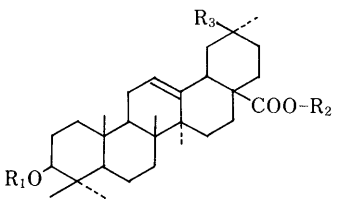
Keywords *Talinum triangulare*; Portulacaceae; saponin; oleanane triterpene; methyl spergulagenate

In continuing our search for chemical constituents of Indonesian medicinal plants, we have studied *Talinum triangulare* WILLD. *Talinum triangulare* is known locally as Ginseng Bugis and is used as a traditional treatment for tonic in Indonesia.

The present paper deals with the isolation and structure elucidation of the saponins.

The dried roots (1.0 kg) of *Talinum triangulare* (Portulacaceae) were extracted with MeOH and the concentrated residue was separated with Et_2O and 1-BuOH, successively. The 1-BuOH extract (7.0 g) was subjected to column chromatography on silica gel by eluting with $CHCl_3$–MeOH–H_2O (30:12:1, 15:6:1, 10:6:1) to give two fractions A and B. Fraction B was separated by chromatography on silica gel ($CHCl_3$: MeOH : H_2O = 30:8:1, 15:6:1) followed by repeated column chromatography on a Lichroprep RP-18 (65% MeOH) affording a new saponin named talinumoside I (**1**) and one known saponin (**2**).

Talinumoside I (**1**) showed an $[M-H]^-$ ion at *m/z* 837 on the negative fast atom bombardment mass spectrum (FAB-MS), indicating its molecular weight to be 838. On acid hydrolysis, **1** afforded glucose and glucuronic acid, while on enzymatic hydrolysis with crude hesperidinase, **1** yielded an aglycone (**3**) which was identified as a known triterpene, methyl spergulagenate.[1] The ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum of **1** revealed the presence of an oxygenated carbon (δ 89.3), a pair of olefinic carbons (δ 123.5, 143.8), two ester carbons (δ 176.1, 177.0) and two anomeric carbons (δ 95.8, 106.6). Comparison of the ^{13}C-NMR spectrum of **1** with that of **3** indicated the presence of glycosylation shifts[2,3] for the signals due to 2-, 3-, and 28-C of the aglycone moiety, disclosing that **1** must be a 3,28-bisdesmoside of **3**, On saponification, **1** yielded a prosapogenin (**4**) and 1,6-anhydroglucose, which is characteristic of β-glucosyl ester of di- and triterpenes.[4] Compound **4** showed one anomeric proton signal at δ 6.28 (1H, d, J=7.9 Hz) and one anomeric carbon signal. The prosapogenin afforded glucuronic acid on acid hydrolysis. Based on these results, **1** can be formulated as shown in Chart 1.



	R_1	R_2	R_3
1	β-glcA	β-glc	COOMe
2	β-glcA	β-glc	CH_3
3	H	H	COOMe
4	β-glcA	H	COOH

Chart 1

Saponin **2** was identified as chikusetsusaponin IVa which has been isolated from rhizomes of *Panax japonicus* C. A. MEYER and many other *Panax* species.[5]

TABLE I. ^{13}C-NMR Chemical Shifts in C_5D_5N

Carbon No.	1	2	3	4
1	38.7	38.7	38.7	38.7
2	26.3	26.3	28.1	26.3
3	89.3	89.2	78.1	89.3
4	39.5	39.5	39.5	39.5
5	55.9	55.9	55.9	55.9
6	18.5	18.5	18.8	18.5
7	33.2	32.6	33.2	33.2
8	39.9	39.9	39.9	39.9
9	48.0	48.0	48.0	48.0
10	37.0	37.0	37.0	37.0
11	23.8	23.4	23.8	23.8
12	123.5	123.5	123.5	123.5
13	143.8	144.1	143.8	143.8
14	42.0	42.2	42.0	42.0
15	28.4	28.3	28.8	28.4
16	23.6	23.8	23.6	23.6
17	46.5	47.0	46.5	46.5
18	43.2	41.8	43.2	43.2
19	42.5	46.3	42.5	43.2
20	44.0	30.8	44.0	44.0
21	30.6	34.1	30.6	31.2
22	34.0	32.6	34.0	34.8
23	28.4	28.3	28.4	28.4
24	17.1	17.1	17.1	17.1
25	15.6	15.6	15.6	15.6
26	17.5	17.5	17.5	17.5
27	26.2	26.2	26.2	26.2
28	177.0	176.5	179.9	180.0
29	28.4	33.2	28.4	29.1
30	176.1	23.6	177.2	179.5
OMe	51.7		51.7	
C-28 G1	95.8	95.8		
G2	74.1	74.1		
G3	79.4	79.3		
G4	71.0	71.1		
G5	78.9	78.9		
G6	61.9	62.3		
C-3 GA1	106.6	106.6		106.6
GA2	75.3	75.3		75.3
GA3	78.3	78.4		78.3
GA4	73.6	73.6		73.6
GA5	76.7	76.6		76.7
GA6	176.1	176.2		176.1

Experimental

Optical rotations were measured with a Union PM-101 automatic digital polarimeter. NMR spectra were recorded on a JEOL GX-400 instrument in C_5D_5N, using tetramethylsilane (TMS) as an internal standard. For gas liquid chromatography (GLC), a Shimadzu GC-6A apparatus was used. Mass spectra (MS) was taken on a JEOL JMS-01-SG-2 spectrometer by the direct inlet method; ionization volatage 75 eV. For column chromatography, Kieselgel 60H (Merck, art. 7736) and Lichroprep RP-18 (25—40 μm, reversed-phase, Merck) were used.

Extraction and Separation of Saponins The roots of *Talinum triangulare* were extracted with hot MeOH. The concentrated MeOH extract was separated Et_2O and 1-BuOH, successively. The 1-BuOH extract was subjected to column chromatography on silica gel by eluting with $CHCl_3$–MeOH–H_2O (30:12:1, 15:6:1, 10:6:1) to give two fractions A and B.

Frtion B was chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (30:8:1, 15:6:1) followed by repeated column chromatography on Lichroprep RP-18 (65% MeOH) affording two saponins, **1** and **2**.

Compound **1**: A white powder, $[\alpha]_D$ +57.5° (c=0.8, C_5H_5N). *Anal.* Calcd for $C_{43}H_{66}O_{16}\cdot 5H_2O$: C, 54.53; H, 8.30. Found: C, 54.53; H, 8.16. Compound **2**: Identification was achieved by comparison of the optical rotation, ^{1}H- and ^{13}C-NMR spectra with those of an authentic sample.

Acid Hydrolysis of 1 A solution of **1** (2 mg) in 10% H_2SO_4 was refluxed for 4 h. The reaction mixture was diluted with H_2O and then extracted with Et_2O. The H_2O layer was neutralized with Amberlite MB-3 ion exchange resin and evaporated to dryness. The resulting monosaccharides were trimethylsilylated with *N*-trimethylsilylimidazole and identified by GLC comparison with authentic samples.

Compound **1** afforded D-glucose and D-glucuronic acid, while a genuine aglycone of this saponin was not obtained owing to the acid-catalyzed modification.

A solution of **1** (10 mg) and crude hesperidinase (Tanabe Pharm. Ind. Co. Ltd., Osaka, 10 mg) in H_2O was incubated at 40 °C for 40 h. After heating at 100 °C for a few minutes, the reaction mixture was extracted with Et_2O. The Et_2O layer afforded an aglycone. This product was identified as methyl spergulagenate from the ^{1}H- and ^{13}C-NMR spectra and other physical constants.

A suspension of **1** (50 mg) in aqueous 5% KOH was heated on a boiling water bath for 2 h. The reaction mixture was neutralized with Amberlite MB-3 resin and then filtered. The filtrate afforded 1,6-anhydroglucose and compound **4** (25 mg). Acid hydrolysis of **4** was carried out by the above mentioned method. Compound **4** yielded D-glucuronic acid.

Acknowledgement We are grateful to Prof. Basri Hasanuddin, Rector of Hasanuddin University.

References

1) I. Kitagawa, K. Kitazawa, K. Aoyama, M. Asanuma, and I. Yoshioka, *Tetrahedron*, **28**, 923 (1972).
2) R. Kasai, M. Suzuo, and O. Tanaka, *Tetrahedron Lett.*, **1977**, 175.
3) R. Kasai, M. Okihara, J. Asakawa, K. Mizutani, and O. Tanaka, *Tetrahedron*, **35**, 1427 (1979).
4) H. Kohda, R. Kasai, K. Yamasaki, K. Murakami, and O. Tanaka, *Phytochemistry*, **15**, 981 (1976).
5) T. D. Lin, N. Kondo, and J. Shoji, *Chem. Pharm. Bull.*, **24**, 253 (1976).