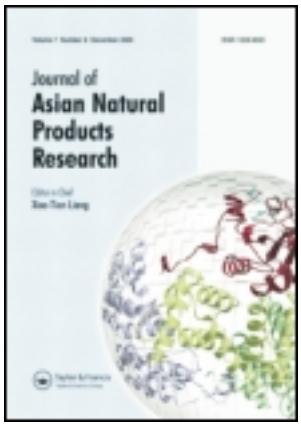

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NEW TIRUCALLANE-TYPE TRITERPENOID SAPONINS FROM *SAPINDUS MUKOROSSI* GAETN.

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Two new tirucallane-type triterpenoid saponins, sapimukoside C (**1**) and sapimukoside D (**2**), have been isolated from the roots of *Sapindus mukorossi* Gaetn. Their structures have been determined, on the basis of spectral and chemical analysis, as 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-[α-L-arabinopyranosyl-(1 → 3)]-β-D-glucopyranosyl (21,23*R*)-epoxyl tirucalla-7,24-diene-(21*S*)-ethoxyl-3β-ol (**1**) and 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-[α-L-arabinopyranosyl-(1 → 3)]-β-D-glucopyranosyl (21,23*R*)-epoxyl tirucall-7, 24-diene-(21*S*)-methoxyl-3β-ol (**2**).

Keywords: *Sapindus mukorossi* Gaetn; Sapindaceae; Tirucallane-type; Triterpenoid saponin; Sapimukoside C; Sapimukoside D

INTRODUCTION

Sapindus mukurossi Gaetn. (Sapindaceae) is a folk medicine used as an expectorant, for relieving coughs, detoxification and defervescence [1]. We have reported previously two new triterpenoid saponins from the roots of this plant [2]. Further study led to the isolation of another two new saponins, sapimukoside C and D (**1** and **2**) (Fig. 1). We herein report their structural elucidation.

RESULTS AND DISCUSSION

Sapimukoside C (**1**) was isolated as a white powder, mp 172–174°C. Negative HR-FABMS gave an $[M-1]^-$ peak at *m/z* 923.5294, corresponding to a molecular formula of $C_{49}H_{80}O_{16}$.

The ^{13}C NMR spectrum of the aglycone moiety of **1** shows signals for seven tertiary methyls, four methine carbons, four quaternary carbons [δ 51.7 (C-14), 44.3 (C-13), 39.8

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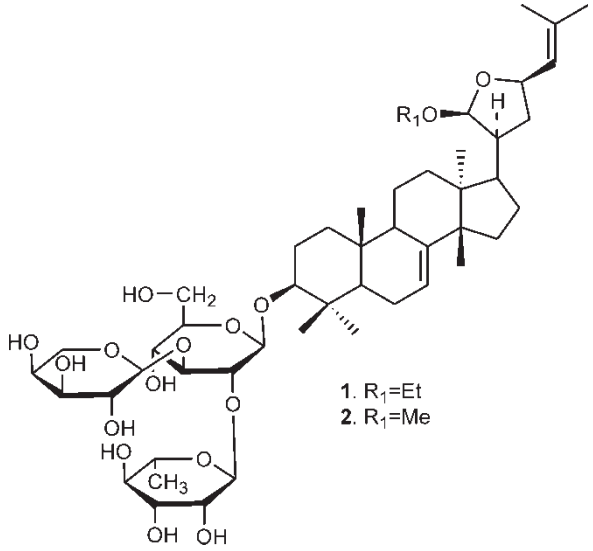

FIGURE 1 Structures of compounds **1** and **2**.

(C-4), 35.1 (C-10)], two trisubstituted olefinic carbons [δ 118.5 (C-7), 145.9 (C-8)], eight methene carbons, and one oxymethine carbon [δ 89.3 (C-3)]. These data are consistent with a tirucallane–euphane system having a double bond between C-7α and C-8, and a 3β hydroxyl group [3–5]. In addition, the ^{13}C and ^{1}H spectra also indicate one hemiacetal carbon [δ 107.3 (C-21)], one oxymethine carbon [δ 75.8 (C-23)], two olefinic carbons [δ 129.4 (C-24), 133.4 (C-25)], which suggest a hemiacetal group and one double bond in the side-chain. Further comparison of the NMR data with those of sapimukoside A [2], 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-[α-L-arabinopyranosyl-(1 → 3)]-β-D-glucopyranosyl-(21,23*R*)-epoxyl tirucall-7,24-diene-3β,21-diol, showed that the two structures are very similar except that **1** has an additional ethoxyl group and C-21 is shifted downfield from 98.0/102.0 to 107.3. These findings suggest that the additional ethoxyl group is linked at C-21 of the aglycone, as is further confirmed by the HMBC spectrum showing a long-range correlation between the methylene proton of the ethoxyl group (δ 4.00, 1H, dq, 7.1, 9.3 Hz; δ 3.61, 1H, dq, 7.1, 9.3 Hz) and C-21. Unlike sapimukoside A [2], the ^{1}H and ^{13}C NMR spectra of the aglycone indicate that the aglycone is not a C_{21} epimeric mixture. Since correlations are observed between Me-18 and H-20, H-20 and H-23, H-21 and H-23, H-24 and the methylene proton of the ethoxyl group in the NOESY spectrum (Fig. 2), the configurations of C-21 and C-23 are *S* and *R* respectively. Hence, the aglycone was determined to be 21,23*R*-epoxyl tirucall-7,24-diene-21*S*-methoxy-3β-ol.

Acid hydrolysis of **1** on TLC yielded glucose, arabinose and rhamnose by comparison with authentic samples. The linkage sites of each sugar were determined by an HMBC spectrum, which shows long-range correlations for H-1″ of the rhamnosyl unit (δ 6.32, 1H, brs) to C-2′ of the glycosyl unit (δ 77.4), H-1‴ of the arabinosyl unit (δ 4.94, 1H, d, $J = 7.4$ Hz) to C-3′ of the glycosyl unit (δ 88.1), and H-1′ of the glycosyl unit (δ 4.85, 1H, d, $J = 7.0$ Hz) to C-3 (δ 89.3) of the aglycone. Each sugar is a pyranosyl with β configuration for glucosyl and α configuration for both rhamnosyl and arabinosyl from the NMR data. Thus, the structure of **1** is elucidated as 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-[α-L-arabinopyranosyl-(1 → 3)]-β-D-glucopyranosyl-(21,23*R*)-epoxyl tirucall-7,24-diene-(21*S*)-ethoxy-3β-ol (**1**), and named sapimukoside C.

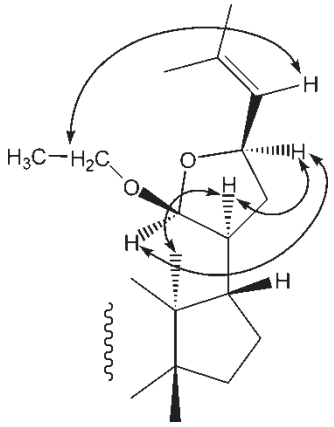

FIGURE 2 Significant NOE effects in the side-chain of **1**.

Sapimukoside D (**2**) was isolated as a white powder, and analyzed for $C_{48}H_{78}O_{16}$ by negative-ion HR-FABMS spectrum. A careful comparison of the ^{1}H and ^{13}C NMR spectra of **2** with those of **1** shows that the two compounds are very similar except for the substituent at C-21. There is a methoxyl group [δ_C 54.9 (q); δ_H 3.58 (3H, s)] in **2** instead of an ethoxyl group. Furthermore, the HMBC spectrum shows long-range correlations between the methyl protons of the methoxyl group and C-21. Thus, the structure of sapimukoside D is 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-[α-L-arabinopyranosyl-(1 → 3)]-β-D-glucopyranosyl-(21,23*R*)-epoxyl tirucall-7,24-diene-(21*S*)-methoxy-3β-ol (**2**).

Interestingly, unlike sapimukosides A and B and other known tirucallane-type triterpenes having a similar hemiacetal side chain [5–9] that exist in the solution as a C-21 epimeric mixture, sapimukosides C and D are pure compounds in solution due to the methoxyl and ethoxyl groups at C-21.

EXPERIMENTAL

General Experimental Procedures

Melting points were measured on a Koffler melting point apparatus produced by Sichuan University (China) and are uncorrected. Optional rotations were measured on a Japanese Fasco DIP-370 digital polarimeter. FABMS and HR-FABMS were recorded on a VG Auto Spec-3000 spectrometer. All NMR experiments were recorded on a Bruker DRX-500 spectrometer at room temperature.

Plant Material

The roots of *Sapindus mukorossi* Gaertn. were collected from Yuxi, Yunnan Province (China) in July 1998 and identified by Professor Li Heng at Kunming Institute of Botany, The Chinese Academy of Sciences.

Extraction and Isolation

The roots (5.9 kg) were extracted with hot EtOH (4 ×) and then concentrated under reduced pressure. The concentrated extract was partitioned between *n*-BuOH and water. The *n*-BuOH layer was subjected to DM 101 column chromatography, eluting with water and 80% EtOH,

TABLE I NMR data of compounds **1** and **2** (C_5D_5N)

1			***2***		
No.	^{13}C	^{1}H	*No.*	^{13}C	^{1}H
1	37.8		1	37.8	
2	27.5[a]		2	27.4[a]	
3	89.3	3.44 (1H, dd, 3.8, 11.8 Hz)	3	89.2	3.43 (1H, dd, 3.7, 11.5 Hz)
4	39.8		4	39.7	
5	52.0	1.37 (1H, dd, 5.7, 11.5 Hz)	5	52.0	1.36 (1H, dd, 5.7, 11.0 Hz)
6	24.5		6	24.3	
7	118.5	5.33 (br s)	7	118.6	5.31 (br s)
8	145.9		8	145.9	
9	49.1	2.25 (1H, d, 10.5 Hz)	9	48.9[a]	2.24 (1H, d, 10.7 Hz)
10	35.1		10	35.0	
11	18.4		11	18.1	
12	32.9		12	32.9	
13	44.3		13	44.2	
14	51.7		14	51.8	
15	34.4		15	34.4	
16	28.3		16	28.3	
17	49.3	1.93 (1H, dd, 6.6, 12.1 Hz)	17	49.2	1.91 (1H, dd, 6.6, 12.1 Hz)
18	23.3	1.06 (3H, s)	18	23.0	1.03 (3H, s)
19	13.6	0.76 (3H, s)	19	13.5	0.74 (3H, s)
20	49.0	2.49 (1H, m)	20	48.9[a]	2.47 (1H, m)
21	107.3	5.18 (1H, d, 1.7 Hz)	21	108.7	5.05 (br s)
22	37.6		22	37.4	
23	75.8	5.09 (1H, dd, 7.0, 14.9 Hz)	23	75.7	5.08 (1H, dd, 6.5,14.0 Hz)
24	129.4	5.63 (1H, dq, 1.1, 8.7 Hz)	24	129.3	5.59 (br d, 8.4 Hz)
25	133.4		25	133.5	
26	26.1		26	25.9	
27	18.2		27	18.0	
28	28.0	1.24[a] (3H, s)	28	27.9	1.23[a] (3H, s)
29	16.2	1.24[a] (3H, s)	29	16.2	1.23[a] (3H, s)
30	27.5[a]	1.02 (3H, s)	30	27.4[a]	0.99 (3H, s)
OCH_2CH_3	16.0	1.29 (3H, t, 7.1 Hz)	OCH_3	54.9	3.58 (3H, s)
OCH_2CH_3	63.3	4.00 (1H, dq, 7.1, 9.3 Hz), 3.61 (1H, dq, 7.1, 9.3 Hz)			
Glc-1′	105.1	4.85 (1H, d, 7.0 Hz)	Glc-1′	105.0[a]	4.85 (1H, d, 7.0 Hz)
2′	77.4	4.14 (1H, m)	2′	77.3	4.16 (1H, m)
3′	88.1	4.15 (1H, m)	3′	88.2	4.17 (1H, m)
4′	70.0	3.94 (1H, t, 8.5 Hz)	4′	70.0a	3.94 (1H, t, 8.5 Hz)
5′	78.0	3.86 (1H, m)	5′	78.0	3.85 (1H, m)
6′	62.7	4.47 (1H, m), 4.25 (1H, m)	6′	62.7	4.47 (1H, m), 4.23 (1H, m)
Rha-1″	101.9	6.32 (1H, br s)	Rha-1″	101.9	6.37 (1H, br s)
2″	72.5[a]	4.79 (1H, d, 3.4 Hz)	2″	72.5[a]	4.79 (1H, br s)
3″	72.6	4.57 (1H, dd, 3.4, 9.4 Hz)	3″	72.6	4.57 1H, dd, 3.7, 9.3 Hz)
4″	73.9	4.28 (1H, m)	4″	73.9	4.28 (1H, m)
5″	70.1	4.70 (1H, dq, 6.2, 9.4 Hz)	5″	70.0a	4.71 (1H, dq, 8.7 Hz)
6″	18.9	1.66 (3H, d, 6.3 Hz)	6″	18.7	1.65 (3H, d, 6.5 Hz)
Ara-1‴	105.0	4.94 (1H, d, 7.4 Hz)	Ara-1‴	105.0[a]	4.92 (1H, d, 7.0 Hz)
2‴	72.5[a]	4.44 (1H, t, 8.0 Hz)	2‴	72.5[a]	4.43 (1H, t, 7.9 Hz)
3‴	74.5	4.09 (1H, dd, 3.4, 9.1 Hz)	3‴	74.4	4.04 (1H, dd, 2.8, 9.0 Hz)
4‴	69.5	4.27 (1H, m)	4‴	69.4	4.25 (1H, m)
5‴	67.8		5‴	67.8	

[a] Signals overlap.

successively. Then the 80% EtOH fraction was repeatedly subjected to silica-gel column chromatography with $CHCl_3$–MeOH (8:2 or 9:1 v/v) and Rp-18 column chromatography with aqueous EtOH to afford **1** (120 mg) and **2** (98 mg).

Sapimukoside A [2], 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-[α-L-arabinopyranosyl-(1 → 3)]-β-D-glucopyranosyl-(21,23*R*)-epoxyl tirucall-7,24-diene-3β,21diol (5 mg) and silica gel (500 mg) were added to MeOH (10 ml) or 90% EtOH. Then the mixture was heated in a boiling water bath under reflux for 2 h. After filtering the silica gel, we checked the filtrate by TLC but did not find **1** or **2** in the solution. Thus compounds **1** and **2** were natural products in *Sapindus mukurossi*.

Sapimukoside C, 3-O-α-L-rhamnopyranosyl-(1 → 2)-[α-L-arabinopyranosyl-(1 → 3)]-β-D-glucopyranosyl-(21,23R)-epoxyl-tirucalla-7, 24-diene-(21S)-ethoxyl-3β-ol (1)

White powder, mp 172–174°C; $[\alpha]_D^{25}$ −6.7 (*c* 0.45, MeOH). Negative FAB-MS (*m/z*): 924 $[M]^-$, HRFAB-MS: 923.5294 $[M-1]^-$ (calcd for $C_{49}H_{79}O_{16}$, 923.5368). For ^1H and ^{13}C NMR see Table I.

Sapimukoside D, 3-O-α-L-rhamnopyranosyl-(1 → 2)-[α-L-arabinopyranosyl-(1 → 3)]-β-D-glucopyranosyl-(21,23R)-epoxyl-tirucalla-7,24-diene-(21S)-methoxyl-3β-ol (2)

White powder, mp 180–182°C; $[\alpha]_D^{25}$ −12.3 (*c* 0.49, MeOH). Negative FAB-MS (*m/z*): 910 $[M]^-$, HRFAB-MS: 909.5220 $[M-1]^-$ (calcd for $C_{48}H_{77}O_{16}$, 909.5212). For ^1H and ^{13}C NMR see Table I.

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