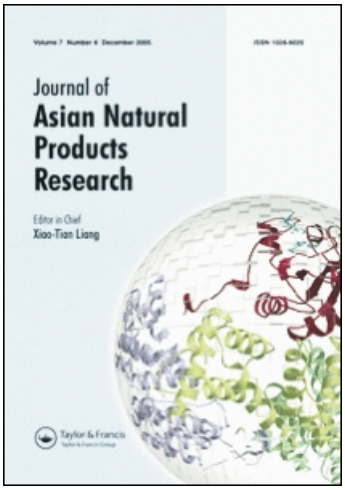


**Journal of Asian Natural Products Research**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

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**To cite this Article** Ni, Wei , Hua, Yan , Teng, Rong-Wei , Kong, Yun-Cheung and Chen, Chang-Xiang(2004) 'New tirucallane-type triterpenoid saponins from *Sapindus mukorossi* Gaetn.', Journal of Asian Natural Products Research, 6: 3, 205 — 209
**To link to this Article: DOI:** 10.1080/1028602032000169613
**URL:** http://dx.doi.org/10.1080/1028602032000169613

*Journal of Asian Natural Products Research*, September 2004, VOL. 6 (3), pp. 205–209



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

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*(Received 25 June 2003; Revised 9 October 2003; In final form 18 October 2003)*



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 [$\delta$ 51.7 (C-14), 44.3 (C-13), 39.8

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ISSN 1028-6020 print/ISSN 1477-2213 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/1028602032000169613

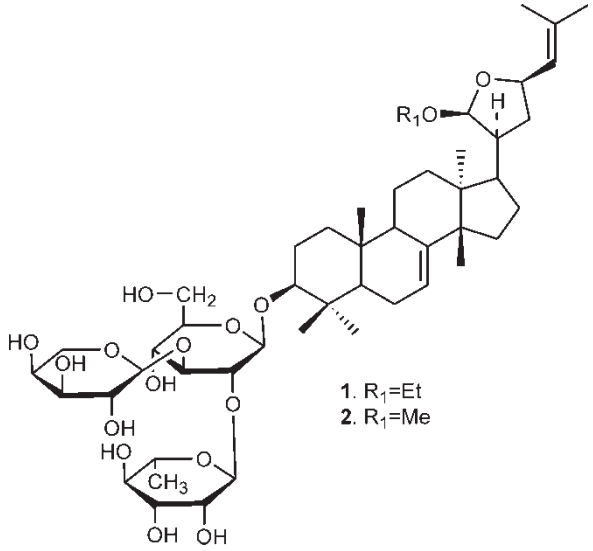


FIGURE 1 Structures of compounds **1** and **2**.

(C-4), 35.1 (C-10)], two trisubstituted olefinic carbons [$\delta$ 118.5 (C-7), 145.9 (C-8)], eight methene carbons, and one oxymethine carbon [$\delta$ 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 [$\delta$ 107.3 (C-21)], one oxymethine carbon [$\delta$ 75.8 (C-23)], two olefinic carbons [$\delta$ 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 ($\delta$ 4.00, 1H, dq, 7.1, 9.3 Hz; $\delta$ 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 ($\delta$ 6.32, 1H, brs) to C-2′ of the glycosyl unit ($\delta$ 77.4), H-1‴ of the arabinosyl unit ($\delta$ 4.94, 1H, d, $J = 7.4$ Hz) to C-3′ of the glycosyl unit ($\delta$ 88.1), and H-1′ of the glycosyl unit ($\delta$ 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.

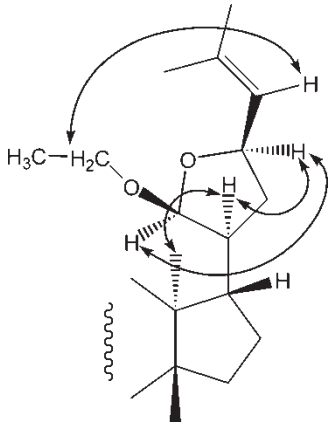


FIGURE 2 Significant NOE effects in the side-chain of **1**.



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 [$\delta_C$ 54.9 (q); $\delta_H$ 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.



***Acknowledgements***

The authors are grateful to Ms Liang Hui-Ling and Wu Yu for measuring the MS spectrum and to Mr Ji Yun-Heng for measuring the optical rotation. This work was financed by the School of Chinese Medicine, the Chinese University of Hong Kong.

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