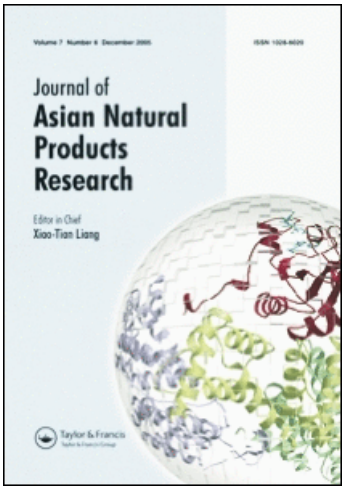


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# Two new triterpenoids from the carpophore of *Xanthoceras sorbifolia* Bunge

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Two new triterpenoids were isolated from the dried carpophore of *Xanthoceras sorbifolia* Bunge (Sapindaceae). By means of spectroscopic data (1D and 2D NMR, ESI-MS) and chemical evidence, their structures were established as 16-*O*-acetyl-21-*O*-(3′,4′-di-*O*-angeloyl)-β-D-fucopyranosyl theasapogenol B (**1**) and 3β,23-dihyroxy-lup-20(29)en-28-oic acid -23-caffeate (**2**).

*Keywords*: Carpophore; *Xanthoceras sorbifolia*; Sapindaceae; Triterpenoid

## 1. Introduction

*Xanthoceras sorbifolia* Bunge (Sapindaceae) is a shrub that grows mainly in Inner Mongolia, China. Its bark and fruits are used as a folk medicine to treat rheumatism and enuresis of children. Previous phytochemical studies on this plant revealed the presence of saponins, flavonoids and sterols [1–4]. The present paper describes the isolation and elucidation of two new triterpenoids from the carpophores of the plant.

## 2. Results and discussion

Compound **1** was isolated as white needles, mp 237–239°C. It showed positive Liebermann–Burchard and Molish reactions. The sugar was identified as fucose by acid hydrolysis [2], and co-TLC with an authentic sample. The HREI-MS spectrum showed a molecular ion peak at *m/z* 842.5181 $[M]^+$, which combined with its $^1$H NMR and $^{13}$C NMR spectra to give the molecular formula of $C_{48}H_{74}O_{12}$. In the $^1$H NMR spectrum of 1, the signals at $\delta$ 1.86 (6H, brs), 1.95 (6H, d, $J = 7.2$ Hz), 5.89 (2H, q, $J = 7.2$ Hz) could be assigned to α-Me, β-Me and β-H of two angeloyl functions which were also supported by the $^{13}$C NMR spectrum of **1** at $\delta$ 167.3, 139.0, 138.9, 127.5, 127.4, 20.8, 20.6, 15.9, 15.8.

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Additionally, the signal at $\delta$ 169.3 attributed to an ester carbonyl and the signal at $\delta$ 22.1 assigned to a methyl group indicated the existence of an acetoxyl group in compound **1**, and this was supported by the $^1$H NMR spectrum at $\delta$ 2.29 (3H, s). Besides that, the $^1$H NMR spectrum also gave seven singlet signals of methyls at $\delta$ 0.81, 0.87, 1.01, 1.27, 1.43, 1.47, 1.84 and the signal of the anomeric proton of fucose at $\delta$ 4.95 (1H, d, $J = 7.8$ Hz), which indicated that the anomer of the fucose was of β orientation. The $^{13}$C NMR data of compound 1 were very close for the known compound D, which was previously isolated from the plant [2]. In particular the signals of B, C, D, E rings and fucose moiety of **1** were fully in agreement with compound D, indicating that **1** was a derivative of 16-*O*-acetyl-21-*O*-(3′,4′-di-*O*-angeloyl)-β-D-fucopyranosyl protoaescigenin. The differences between **1** and compound D are as follows. There are seven methyl signals in **1** instead of six methyls in compound D based on the $^1$H NMR analysis of **1**. On the other hand, one carbinol group is missing in **1** as compared with compound D according to the $^{13}$C NMR data. Furthermore, a comparison of the $^{13}$C NMR data for **1** with those of compound D showed that an upfield shift of the C-24 signal by 48 ppm (from 64.5 in compound D to 16.6 in **1**) and carbon signals of C-3, C-4 in ring A of 1 were shifted upfield, suggesting the absence of the OH group at C-24 in **1**.

In the HMBC spectrum (figure 1), the correlations between H-24 ($\delta$ 1.01) and C-3 ($\delta$ 77.9), C-5 ($\delta$ 55.7) also indicated that C-24 of compound **1** was not hydroxylated. The long-range correlations between H-21 ($\delta$ 4.21) and C-1′ ($\delta$ 105.9), as well as H-1′ ($\delta$ 4.91) and C-21 ($\delta$ 90.6) indicated that the fucose moiety was linked to the aglycone at C-21. In addition, H-3′ ($\delta$ 5.67), H-4′ ($\delta$ 5.72) presented long-range correlations with $\delta$ 167.3, which indicated that the two angeloyl groups were substituted to the fucose at C-3′ and C-4′, respectively. Furthermore, a long-range correlation between H-16 ($\delta$ 5.96) and *C*OMe ($\delta$ 169.3) was observed, so the acetoxyl group must be at C-16. With the data above, the structure of **1** was established as 16-*O*-acetyl-21-*O*-(3′,4′-di-*O*-angeloyl)-β-D-fucopyranosyl theasapogenol B.

Compound **2** was isolated as yellow needles, mp 246–248°C. The HREI-MS spectrum showed a molecular ion peak at *m/z* 634.3869 $[M]^+$, corresponding to the molecular formula of $C_{39}H_{54}O_7$.The $^1$H NMR spectrum revealed the presence of three aromatic protons

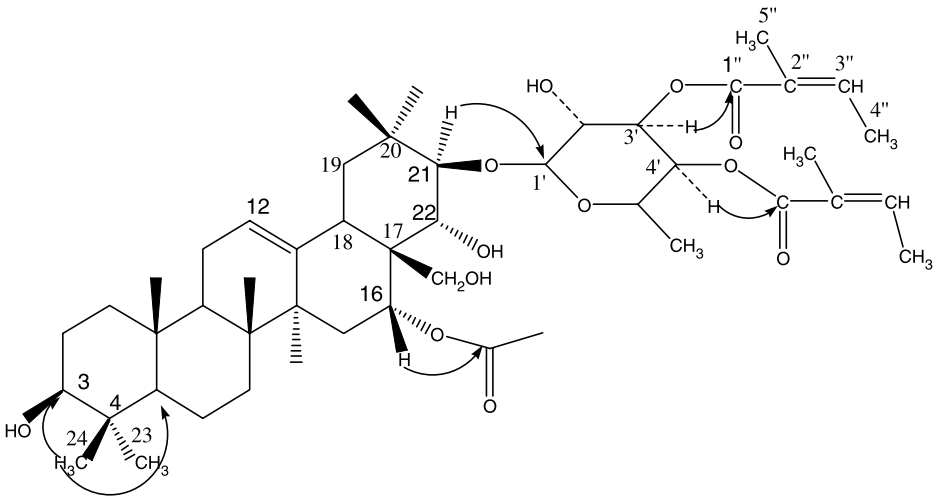


Figure 1. The important HMBC correlations for compound **1**.

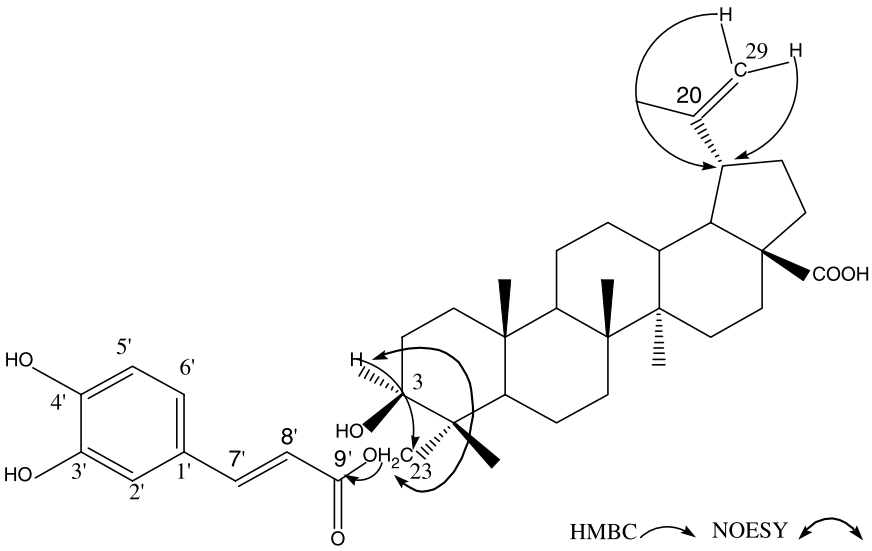


Figure 2. The important HMBC and NOESY correlations for compound **2**.

at $\delta$ 6.80 (1H, d, $J = 8.1$ Hz), 6.99 (1H, d, $J = 8.1$ Hz), 7.05 (1H, s) and a *trans*-double bond signal at $\delta$ 7.47 (1H, d, $J = 15.9$ Hz), 6.25 (1H, d, $J = 15.9$ Hz) in good agreement with signals of authentic caffeic acid. The $^1$H NMR spectrum also displayed five methyl signals at $\delta$ 0.65, 0.82, 0.87, 0.87, 1.64 (3H, each, Me). Additionally, the signals at $\delta$ 4.69 (1H, s), 4.56 (1H, s) in $^1$H NMR and $\delta$ 109.7 (C-29), 150.4 (C-20) in $^{13}$C NMR showed the presence of an isopropylidene group. Furthermore, two oxygen-bearing carbons at $\delta$ 70.2 (C-3), 65.2 (C-23) could be observed in $^{13}$C NMR, which indicated that the triterpenoid moiety was a derivative of betulinic acid. In the NOESY spectrum of 2 (figure 2), a correlation between H-3, $\delta$ 3.42 and H-23 ($\delta$ 3.94) could be observed. From the above data and the HMQC experiment of 2, it can be identified to be a caffeic acid ester of 23-hydroxy-betulinic acid.

In the HMBC spectrum (figure 2), the correlation between H-3 ($\delta$ 3.42) and C-23 ($\delta$ 65.2), together with the correlation between H-23 ($\delta$ 3.94) and C-9′ ($\delta$ 166.4), indicated that the caffeic acid moiety must be linked to the triterpenoid at C-23. With the data above, the structure of 2 was established as 3β,23-dihyroxy-lup-20(29)en-28-oic acid-23-caffeate.

## 3. Experimental

### *3.1 General experimental procedures*

Melting points were measured on a Yanaco micro-hot-stage apparatus and are uncorrected. The UV spectra were recorded on a Shimadzu-2201 spectrometer. The IR (KBr) spectra were measured on a Bruker-IFS-55 spectrometer. 1D and 2D NMR spectra were recorded on a Bruker-ARX-300 or an AV-600 spectrometer, using TMS as an internal standard. ESI-MS was determined by Finnigan LCQ spectrometer. The chromatographic silica gel (200–300 mesh) was produced by the Qingdao Ocean Chemical Factory. Macroporous resin HPD100 was produced by the Hebei Cangzhou Baoen Chemical Factory.

Table 1. $^{1}$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) data of compounds **1** and **2**.

| *1 (in pyridine-$d_5$)* | | | *2 (in DMSO-$d_6$)* | | |
|---|---|---|---|---|---|
| *No.* | $\delta_C$ | $\delta_H$ | *No.* | $\delta_C$ | $\delta_H$ |
| 1 | 39.2 | | 1 | 40.3 | |
| 2 | 28.7 | | 2 | 26.7 | |
| 3 | 77.9 | 3.40 (1H, dd, $J = 5.7$ Hz, $J = 9.9$ Hz) | 3 | 70.2 | 3.42 (1H, t) |
| 4 | 39.4 | | 4 | 41.6 | |
| 5 | 55.7 | | 5 | 47.7 | |
| 6 | 18.6 | | 6 | 17.8 | |
| 7 | 33.1 | | 7 | 33.7 | |
| 8 | 40.1 | | 8 | 40.4 | |
| 9 | 47.1 | | 9 | 50.3 | |
| 10 | 37.2 | | 10 | 36.6 | |
| 11 | 23.8 | | 11 | 21.1 | |
| 12 | 124.6 | | 12 | 25.1 | |
| 13 | 141.8 | | 13 | 38.8 | |
| 14 | 39.0 | | 14 | 42.0 | |
| 15 | 31.3 | | 15 | 29.2 | |
| 16 | 70.5 | 5.96 (1H, d, $J = 7.2$ Hz) | 16 | 31.8 | |
| 17 | 47.1 | | 17 | 55.5 | |
| 18 | 41.4 | | 18 | 48.6 | |
| 19 | 47.9 | | 19 | 46.7 | |
| 20 | 37.1 | | 20 | 150.4 | |
| 21 | 90.6 | 4.21 (1H, d, $J = 9.8$ Hz) | 21 | 30.2 | |
| 22 | 71.9 | 4.67 (1H, d, $J = 9.8$ Hz) | 22 | 37.7 | |
| 23 | 27.1 | 1.47 (3H, s) | 23 | 65.2 | 3.94 (2H, brs) |
| 24 | 16.6 | 1.01 (3H, s) | 24 | 12.2 | 0.65 (3H, s) |
| 25 | 16.0 | 0.87 (3H, s) | 25 | 16.3 | 0.82 (3H, s) |
| 26 | 16.8 | 0.81 (3H, s) | 26 | 15.8 | 0.87 (3H, s) |
| 27 | 28.1 | 1.84 (3H, s) | 27 | 14.3 | 0.87 (3H, s) |
| 28 | 64.3 | 3.95 (1H, d, $J = 10.2$ Hz) | 28 | 177.3 | |
| \ | | 3.63 (1H, d, $J = 10.2$ Hz) | | | |
| 29 | 29.9 | 1.43 (3H, s) | 29 | 109.7 | 4.69 (1H, brs) |
| | | | | | 4.56 (1H, brs) |
| 30 | 19.5 | 1.27 (3H, s) | 30 | 19.0 | 1.64 (3H, s) |
| Fuc. | | | 1′ | 125.6 | |
| 1′ | 105.9 | 4.95 (1H, d, $J = 7.8$ Hz) | 2′ | 114.8 | 7.05 (1H, s) |
| 2′ | 69.9 | | 3′ | 144.8 | |
| 3′ | 74.2 | 5.67 (1H, d) | 4′ | 148.4 | |
| 4′ | 70.9 | 5.72 (1H, d) | 5′ | 115.8 | 6.80 (1H, d, $J = 8.1$ Hz) |
| 5′ | 69.6 | | 6′ | 121.3 | 6.99 (1H, d, $J = 8.1$ Hz) |
| 6′ | 16.3 | 1.20 (3H, d, $J = 6.3$ Hz) | 7′ | 145.7 | 7.47 (1H, d, $J = 15.9$ Hz) |
| Ang. | | | 8′ | 114.3 | 6.25 (1H, d, $J = 15.9$ Hz) |
| 1″ | 167.3 | | 9′ | 166.4 | |
| | 167.3 | | | | |
| 2″ | 127.5 | | | | |
| | 127.4 | | | | |
| 3″ | 139.0 | 5.89 (1H, q, $J = 7.2$ Hz) | | | |
| | 138.9 | 5.89 (1H, q, $J = 7.2$ Hz) | | | |
| 4″ | 20.8 | 1.86 (3H, brs) | | | |
| | 20.6 | 1.86 (3H, brs) | | | |
| 5″ | 15.9 | 1.95 (3H, d, $J = 7.2$ Hz) | | | |
| | 15.8 | 1.95 (3H, d, $J = 7.2$ Hz) | | | |
| Ac. | | | | | |
| *C*OMe | 169.3 | | | | |
| CO*Me* | 22.1 | 2.29 (3H, s) | | | |

### *3.2 Plant material*

The carpophores of *Xanthoceras sorbifolia* Bunge were collected at Shenhe district, Shenyang, China and were identified by Professor Bai-Zhen Yang. A voucher specimen (No. 0187512) is deposited in the Herbarium Department of the Institute of Applied Ecology, Chinese Academy of Sciences.

### *3.3 Extraction and isolation*

Dried carpophores of *Xanthoceras sorbifolia* Bunge (10 kg) were extracted with 70% ethanol. The extract (800 g) was concentrated *in vacuo*, then half of the extract was eluted with $H_2O$, 70% ethanol and 95% ethanol on macroporous resin. The 95% ethanol fraction (16.0 g) was subjected to column chromatography on silica gel gradient eluted with petroleum ether/acetone. Fraction 15 [petroleum ether/acetone (100:16), 600 mg] was rechromatographed on Sephadex LH-20 eluted with MeOH to give compound **1** (7.0 mg); fraction 18 [petroleum ether/acetone (100:22), 1.2 g] was rechromatographed on Sephadex LH-20 eluted with MeOH to give compound **2** (53 mg).

**3.3.1 Compound 1**. White needles (MeOH), mp 237–239°C. $[\alpha]_D^{24}$ + 34.5 (*c* 0.02, MeOH). UV (MeOH) $\lambda_{max}$: 222 nm. IR (KBr) $\nu_{max}$ ($cm^{-1}$): 3438, 2926, 1726, 1642, 1457, 1381, 1237, 1157, 1065, 849. HREI-MS: *m/z* 842.5181 $[M]^+$ (calcd for $C_{48}H_{74}O_{12}$, 842.5189). ESI-MS: *m/z* 865.5 $[M + Na]^+$, 841.5 $[M - H]^-$. $^1H$ NMR and $^{13}C$ NMR data are given in table 1.

**3.3.2 Compound 2**. Yellow needles ($Me_2CO$), mp 246–248°C. $[\alpha]_D^{24}$ + 12.8 (*c* 0.42, $Me_2CO$). UV (MeOH) $\lambda_{max}$: 329, 243. IR (KBr) $\nu_{max}$ ($cm^{-1}$): 3421, 2942, 1695, 1604, 1515, 1448, 1271, 1176, 1024, 882, 814. HREI-MS: *m/z* 634.3869 $[M]^+$ (calcd for $C_{39}H_{54}O_7$, 634.3877). ESI-MS: *m/z* 669.2 $[M + Cl]^-$, 633.3 $[M - H]^-$. $^1H$ NMR and $^{13}C$ NMR data are given in table 1.

### *3.4 Acid hydrolysis of compound 1*

Compound **1** (5 mg) was refluxed in a mixture of conc. HCl/$H_2O$/EtOH (2:1:2) (10 ml) in a water bath for 2 h. The hydrolysate was partitioned between EtOAc and $H_2O$, and the aqueous layer was compared with authentic samples on TLC with silica gel [BAW (4:1:5), upper phase], which showed the sugar was fucose.

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