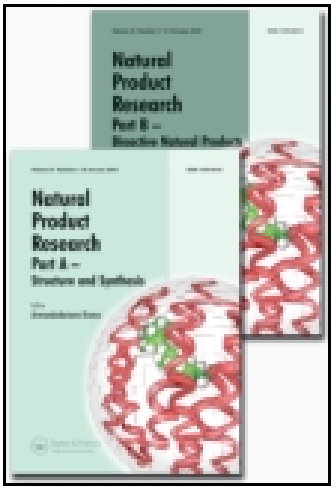

Natural Product Research: Formerly Natural Product Letters
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gnpl20

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Published online: 09 Sep 2010.

To cite this article: Zhao-Wei Yan, Jin-Ping Liu, Dan Lu, Paul Groundwater, Chun-Yan He & Ping-Ya Li (2010) A new 3,4-seco-lupane-type triterpenoid from the pulp of Acanthopanax senticosus (Rupr. et Maxim) Harms, Natural Product Research: Formerly Natural Product Letters, 24:16, 1523-1527, DOI: 10.1080/14786419.2010.485304

To link to this article: http://dx.doi.org/10.1080/14786419.2010.485304

Natural Product Research
Vol. 24, No. 16, 10 October 2010, 1523–1527

A new 3,4-seco-lupane-type triterpenoid from the pulp of *Acanthopanax senticosus* (Rupr. et Maxim) Harms

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(*Received 4 November 2009; final version received 10 April 2010*)

A new triterpenoid, 3,4-seco-lupane-20(29)-ene-3,28-dioic acid (**1**), together with three known lignans, (−)-schisandrin B (**2**), (−)-sesamin (**3**) and (−)-syringaresinol (**4**), was isolated from the pulp of *Acanthopanax senticosus* (Rupr. et Maxim) Harms. Their structures were elucidated by means of physicochemical properties and spectroscopic methods (1D, 2D-NMR and MS).

Keywords: *Acanthopanax senticosus* (Rupr. et Maxim) Harms; 3,4-seco-lupane-type triterpenoid; 3,4-seco-lupane-20(29)-ene-3,28-dioic acid; lignans

1. Introduction

Acanthopanax senticosus (Rupr. et Maxim) Harms is a medicinal plant and belongs to the Araliaceae family, which is widely distributed in the Changbai Mountains of Jilin Province, PR China (Wang, Shan, Ma, & Bao, 2003). *Acanthopanax senticosus* has long been used as a folk medicine to treat diabetes, tumours, hypertension and cerebrovascular diseases. Studies have shown that triterpenoids and lignans are the active constituents of the plant, playing an essential role in the treatment of diseases (Chen, Song, & Guo, 2002). At present, most of the chemical and pharmacological studies are mainly focused on the leaves and roots of *Acanthopana senticosus*, and only a few reports relate to the pulp. Our group has previously reported a study of liposoluble components in the pulp by GC-MS methods (Yan, Zhou, Liu, Lu, & Li, 2009), and as a continuation of our investigation of new active constituents from the pulp of *A. senticosus*, we now report the isolation and structure elucidation of a new triterpenoid, 3,4-seco-lupane-20(29)-ene-3,28-dioic acid (**1**), along with three known lignans, (−)-schisandrin B (**2**), (−)-sesamin (**3**) and (−)-syringaresinol (**4**), in this article.

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ISSN 1478–6419 print/ISSN 1029–2349 online

DOI: 10.1080/14786419.2010.485304
http://www.informaworld.com

2. Results and discussion

Compound **1** was isolated as a white amorphous powder, m.p. 264.7–265.7°C, HR-ESI–MS showed a quasi-molecular ion peak $[M-H]^-$ at m/z 485.32505 (Calcd 485.32725), suggesting the molecular formula to be $C_{30}H_{46}O_5$.

The ^{1}H-NMR spectrum of **1** displayed signals for six tertiary methyl groups at δ0.90 (3H, s), 0.94 (3H, s), 1.04 (3H, s), 1.10 (3H, s), 1.27 (3H, s) and 1.63 (3H, s), two geminal olefinic protons at δ4.56 (1H, br s) and 4.66 (1H, br s), and one oxygen-bearing methine proton at δ3.91 (1H, dd, $J = 12.0$, 2.5 Hz).

The ^{13}C-DEPTQ NMR spectrum of **1** provided 30 carbons: two carbonyl carbons (δ173.6 (C-3) and 180.1 (C-28)), two olefinic carbons (δ150.0 (C-20) and 110.1 (C-29)), two oxygenated carbons (δ83.8 (C-1), 83.7 (C-4)), six methyl carbons (δ24.2 (C-23), 32.4 (C-24), 19.0 (C-25), 16.8 (C-26), 14.8 (C-27), 19.3 (C-30)), and 18 other carbon signals. By analysing the ^{1}H-NMR and ^{13}C-DEPTQ NMR spectra of compound **1**, in particular, the two disubstituted olefinic protons at δ4.56 (1H, br s) and δ4.66 (1H, br s) together with the two olefinic carbons at δ150.0 and 110.1, suggested that compound **1** possessed the characteristic structure of a lupane-type triterpenoid (Figure 1).

The HMBC spectrum (Figure 1), showed important long-range correlations between H-23/C-4; H-24/C-4; H-1/C-4, C-3; H-2a, H-2b/C-3 and C-1; H-30/C-20. With further analysis of the HSQC and DEPTQ 135 spectra of compound **1**, the assignment of the proton and carbon NMR signals above were confirmed unambiguously. Therefore, compound **1** was deduced to be a 3,4-seco-lupane-type triterpenoid. When compared with a previously-reported compound, 11-deoxyisochiisanoside (Yoshizumi et al., 2006), except for the difference due to compound **1** lacking a sugar moiety in the C-28 position, the other chemical shifts were very similar. Moreover, the relative configuration of **1** was also deduced to be the same as that of 11-deoxyisochiisanoside by the further analysis of its nuclear Overhauser effect spectroscopy (NOESY) spectrum; these facts indicated that **1** was the aglycone of 11-deoxyisochiisanoside. Thus, taking all these spectral data into account, compound **1** was elucidated as 3,4-seco-lupane-20(29)-ene-3,28-dioic acid, which has not been reported previously.

The three known lignans were identified as (−)-schisandrin B (Tan, Li, & Fang, 1984), (−)-sesamin (Li & Min, 2004) and (−)-syringaresinol (Jeong et al., 2007), respectively, by analysing their NMR spectra and comparing them with previously reported data.

3. Experimental

3.1. *General experimental procedures*

Melting points were determined on a WRS-1B Digital Point apparatus (Shanghai, China) and were uncorrected. High-resolution ESI mass spectra were recorded on an API Qstar Pulsar instrument. NMR spectra were taken in $CDCl_3$ on a Bruker Avance 500 (Germany) spectrometer, with TMS as the internal standard. Silica gel (200–300 mesh) for chromatography was produced by Qingdao Ocean Chemical Group Co. Ltd., China.

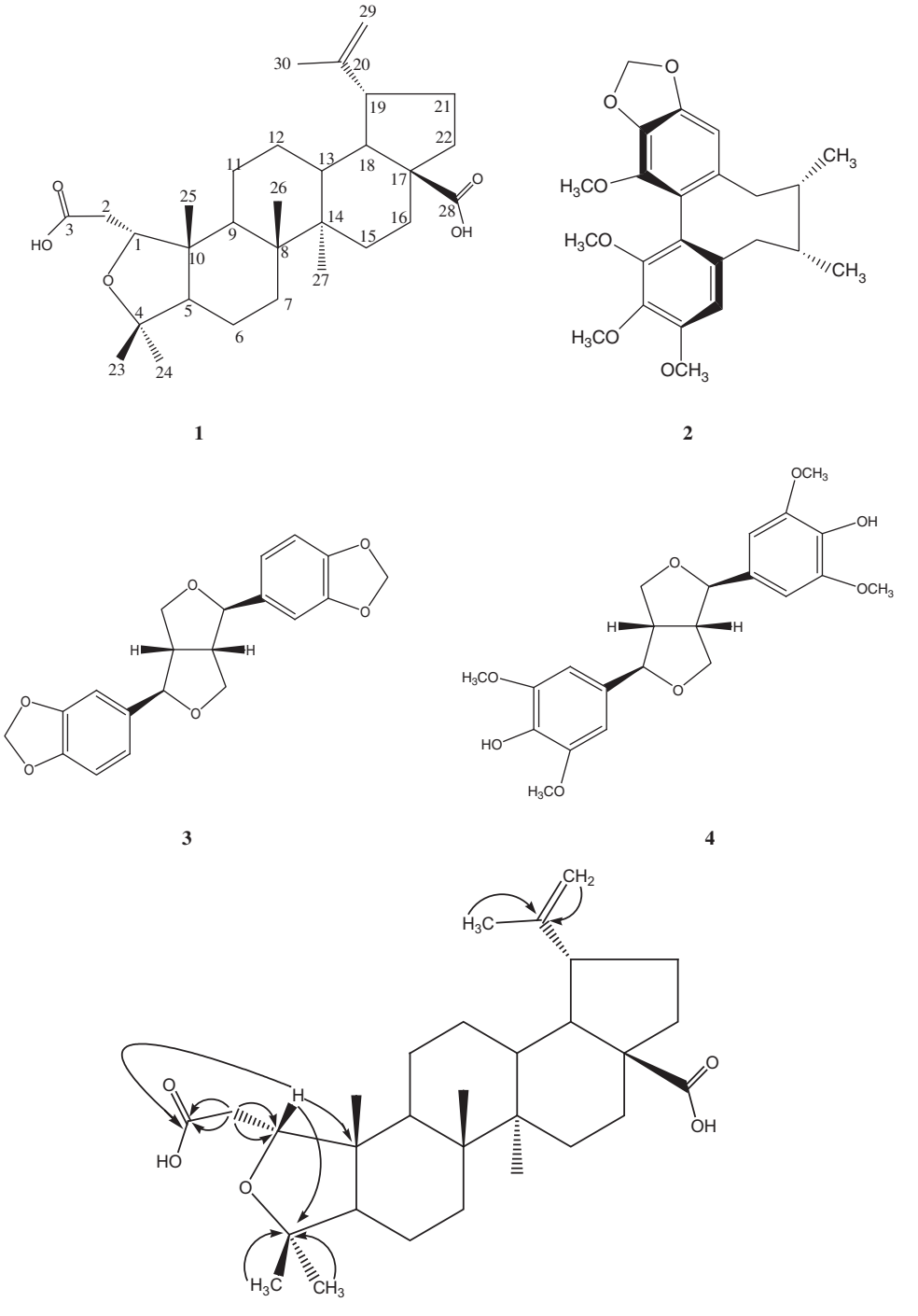

Figure 1. The structures of compounds **1**, **2**, **3**, **4** and key HMBC correlations of **1**.

3.2. *Material*

The fruit of *A. senticosus* was collected in October 2007 in Jingyu County, Jilin Province, PR China, and was authenticated by Professor Jingmin Zhang of Jilin University. A voucher specimen (no. 101) was deposited at the Institute of Frontier Medical Science of Jilin University.

3.3. *Extraction and isolation*

The seeds were carefully removed from the fruit of *A. senticosus* and the remaining parts were collected as the pulp of *A. senticosus*. The pulp (2 kg) was extracted with water (for two days each time, three times) at room temperature. The extracts were combined and concentrated under reduced pressure, followed by the addition of three equivalents of ethanol to make the final ethanol concentration approximately 75% of the total volume (v/v), in order to precipitate proteins, polysaccharides and other macromolecules. The total solution was filtered and the residue removed. The collected ethanol filtrate was evaporated under reduced pressure to give an extract (700 g), which was then suspended in water, and successively extracted with petroleum ether, $CHCl_3$, EtOAc and *n*-BuOH. The petroleum ether extract (27 g) was subjected to silica gel chromatography column, eluting with petroleum ether : acetone (30 : 1–1 : 1) to give eight fractions: fractions 2, 4 and 7 were further purified by silica gel chromatography column to afford compounds **2** (80 mg), **3** (260 mg) and **1** (85 mg), respectively. The $CHCl_3$ extract (90 g) was also subjected to silica gel chromatography column, eluting with petroleum ether : acetone (10 : 1–1 : 1) to give four fractions: fraction 3 was purified over silica gel chromatography column to afford compound **4** (94 mg) (Figure 1).

3.4. *Structure and identification*

3.4.1. *3,4-seco-lupane-20(29)-ene-3,28-dioic acid (**1**)*

White amorphous powder, m.p. 264.7–265.7°C. HR-ESI–MS: $[M-H]^-$ at *m/z* 485.32505 (Calcd 485.32725). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.90 (3H, s, Me-27), 0.94 (3H, s, Me-26), 1.04 (3H, s, Me-25), 1.10 (3H, s, Me-23), 1.27 (3H, s, Me-24), 1.63 (3H, s, Me-30), 2.29 (1H, dd, $J = 15.5$, 2.5 Hz, H-2a), 2.42 (1H, dd, $J = 15.5$, 12.0 Hz, H-2b), 2.90 (1H, m, H-19), 3.91(1H, dd, $J = 12.0$, 2.5 Hz), 4.56 (1H, br s, H-29a) and 4.66 (1H, br s, H-29b); ^{13}C-NMR (DEPTQ; 125 MHz, $CDCl_3$): δ 14.8 (C-27), 16.8 (C-26), 18.5 (C-6), 19.0 (C-25), 19.3 (C-30), 23.7 (C-11), 24.2 (C-23), 25.0 (C-12), 29.9 (C-15), 30.4 (C-21), 32.2 (C-16), 32.4 (C-24), 34.1 (C-7), 35.8 (C-2), 37.1 (C-22), 38.6 (C-13), 41.2 (C-14), 42.1 (C-9), 42.9 (C-8), 46.9 (C-19), 47.9 (C-10), 49.1 (C-18), 55.9 (C-5), 56.1 (C-17), 83.7 (C-4), 83.8 (C-1), 110.1 (C-29), 150.0 (C-20), 173.6 (C-3) and 180.1 (C-28).

Acknowledgement

The authors thank the Analytical Detective Center of Jilin University for recording NMR spectra.

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