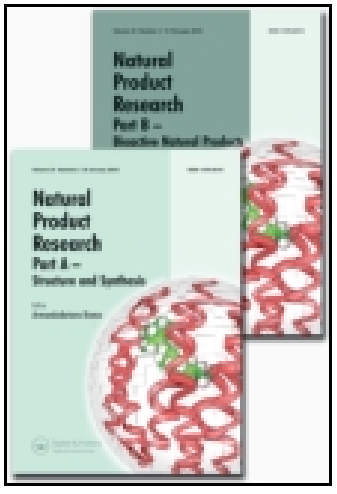

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A new hexenol glycoside from leaves of *Smallanthus sonchifolius*

Xiang Zheng[a], Gai Kuo[a], Dou De-Qiang[a]*, Chen Gui-Rong[a], Kang Ting-Guo[a], Shi Yu-Yuan[a], Li Xing-Tai[b] and Dong Feng[c]

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A new hexenol glycoside with two known compounds was isolated from the leaves of *Smallanthus sonchifolius*. The structure of the new compound was elucidated as Z-hex-3-en-1-ol *O*-alpha-L-arabinopyransyl (1″-2′)-beta-D-glucopyranoside (**1**) on the basis of spectroscopic analysis and chemical evidence. The two known compounds were identified as *ent*-15β-hydroxy-kaur-16-en-19-oic acid (**2**) and *ent*-18-hydroxy-kaur-16-en-19-oic acid (**3**) by comparison of their spectral data with the reported data. Compounds **2** and **3** were isolated for the first time from the title plant.

Keywords: *Smallanthus sonchifolius*; hexenol glycoside; kaurenoic acid

1. Introduction

Yacon, *Smallanthus sonchifolius* (Poepp. & Endl.) H. Robinson, an indigenous plant of the Andes belonging to the family Asteraceae, was introduced into China via Japan in the early 1990s. Usually, yacon is cultivated as a root vegetable, and recent research has revealed that its leaf extract has potential antidiabetic effects (Aybar, Sanchez, Grau, & Sanchez, 2001). Chemical investigations of yacon have revealed that yacon leaves contain various compounds. Phenolics were found in both tubers and leaves of yacon, in which chlorogenic acid and caffeic acid displayed antioxidant activity (Sumio, Kikuo, & Akira, 2006). Diterpenoids and melampolides derivates were isolated from yacon (Consolacion, Ragasa, Alimboyoguen, & Dennis, 2008; Karin, Irmgard, & Fernando, 2007; Katerina & Jitka, 2003; Qiu, Kang, & Dou, 2008), which has a physiological role in the pest-resistant and antimicrobial activity of this plant (Kakuta, Seki, Hashidoko, & Mizutani, 1992; Lin, Hasegawa, & Kodama, 2003). Polyunsaturated fatty acids (PUFAs), smallanthaditerpenic acids and octadecatrienoic acids were isolated from the leaves of yacon cultivated in China (Dou, Tian, & Qiu, 2008; Xiang, Gai, Dou, & Kang, 2009), which possesses a potential ability of antidiabetes. Other components, such as saccharides and essential oils were also confirmed in yacon (Katerina & Jitka, 2003).

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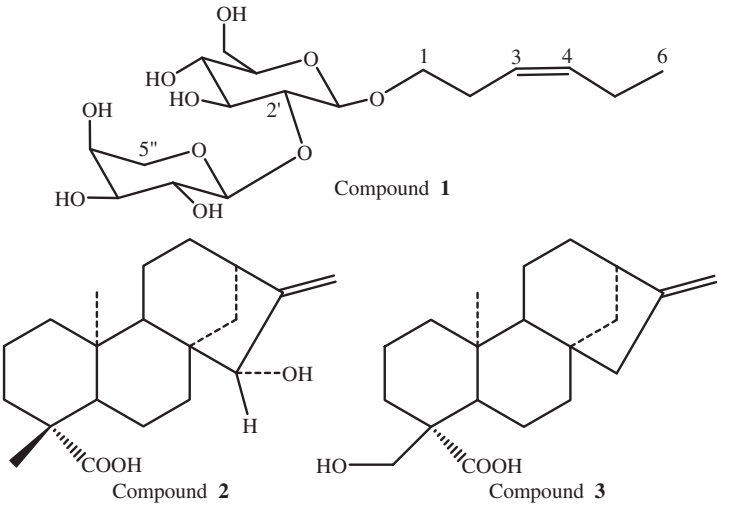

Figure 1. Structures of the components isolated from the leaves of *S. sonchifolius*.

This article deals with the isolation and structure elucidation of the new compound, named Z-hex-3-en-1-ol *O*-alpha-L-arabinopyransyl (1″-2′)-beta-D-glucopyranoside (**1**), together with two known compounds isolated for the first time from the leaves of *S. sonchifolius* (Figure 1).

2. Results and discussion

Compound **1** was isolated as an white amorphous powder. ESI–MS gave its quasi-molecular ion peak at m/z 417 $[M+Na]^+$, and the molecular formula of **1** was determined as $C_{17}H_{30}O_{10}$ by the HR-ESI–MS at m/z 417.4027 $[M+Na]^+$, (calcd 417.4039), as well as from its NMR spectroscopic data, which were assigned using 1-D and 2-D techniques: heteronuclear single quantum coherence (HSQC); heteronuclear multiple-bond correlation (HMBC); and correlation spectroscopy (COSY). Two olefinic protons emerged in the high frequency of the ^{1}H-NMR spectrum at δ 5.43 (1H, dt, $J=6.6$ Hz, 11.4 Hz), 5.39 (1H, dd, $J=6.6$ Hz, 11.4 Hz). Taking into consideration the two tertiary-carbon signals found in the high frequency of ^{13}C-NMR and DEPT spectra, the molecule was believed to contain one –CH=CH– fragment with (*Z*)-configuration, as indicated by the coupling constant ($J_{H3-H4}=11.4$ Hz). The proton signals at δ 3.88 (1H, overlapped) and 3.55 (1H, overlapped) in the ^{1}H-NMR spectrum, in addition to the carbon signal at δ 70.5, revealed the presence of one $-CH_2-O-$fragment. A methyl signal was found at δ 0.96 (3H, t $J=7.8$ Hz) in ^{1}H-NMR spectrum and δ 14.7 in the ^{13}C-NMR spectrum. The carbon signals at δ 21.5, 28.8 in the ^{13}C-NMR and DEPT spectra belonged to two methylene groups. On acid hydrolysis, it yielded a glucose and an arabinose, which were identified by TLC comparison with standard samples of glucose and arabinose, and the absolute configuration of sugar was also determined. Full details are presented in Section 3. From the ^{1}H-, ^{13}C-NMR and DEPT spectra, **1** was proposed

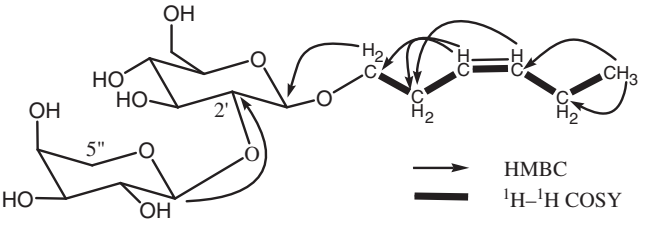

Figure 2. Structure and key ^{1}H–^{1}H COSY and HMBC correlations of compound **1**.

to be a α-L-arabinopyranosyl, β-D-glucopyranoside and an aglycone with *cis*-3-hexenol. The configuration of the two anomeric protons at δ 4.40 (1H, d, $J = 7.8$ Hz), 4.53 (1H, d, $J = 6.6$ Hz) in the ^{1}H-NMR spectrum were determined to be β and α on the basis of the coupling constant. Signals of β-D-glucopyranoside (δ 103.1, 83.2, 77.7, 71.4, 77.9 and 62.6), and α-L-arabinopyranosyl (δ 105.6, 73.1, 74.0, 69.2 and 66.8) were observed in the ^{13}C-NMR spectrum. The HMBC correlations between H-1′ (δ 4.40) of glucose and C-1 (δ 70.5), and between H-1 (δ 3.88; 3.55) and C-1′ (δ 103.1) of glucose showed that the glucose unit was linked at C-1. HMBC correlations between H-1″ (δ 4.53) of arabinose and C-2′ (δ 83.2) of glucose, and between H-2′ (δ 3.36) of glucose and C-1″ (δ 105.6) of arabinose showed that the arabinose unit was linked at C-2′ of glucose (Figure 2). Following the above evidence, the structure of **1** was determined to be Z-hex-3-en-1-ol *O*-alpha-L-arabinopyransyl (**1**″–**2**′)-beta-D-glucopyranoside, and the NMR spectra data are shown in Table 1.

Compounds **2** and **3** were identified as *ent*-15β-hydroxy-kaur-16-en-19-oic acid (**2**) and *ent*-18-hydroxy-kaur-16-en-19-oic acid (**3**) on the basis of their spectroscopic data (Ferinand, Knoll, & Harold, 1980; Lobitz, Tamayo-Castillo, Poveda, & Merfort, 1998).

3. Experimental

3.1. *General experimental procedures*

Optical rotations were measured on a Perkin Elmer digital polarimeter, USA. Nuclear magnetic resonance (NMR) spectra were recorded with transcranial magnetic stimulation (TMS) as an internal standard on a Brucker AVANCE 500 FT-NMR spectrometer. Electrospray ionisation–mass spectrometry (ESI–MS) was measured on an Agilent 1100 LC/MSD Trap-SL spectrometer, USA. Column chromatography was performed on silica gel (200–300 mesh) (Marine Chemical Factory, Qingdao, China) and high performance liquid chromatography (HPLC) was performed with a Hitachi LC-7100 chromatograph apparatus using an octadecylsilyl (ODS) column (YMC-Pack ODS-A) and detected with a UV detector.

3.2. *Materials*

The *S. sonchifolius* leaves were collected in Liaoning Province, P.R. China, and were identified by Prof. Kang Tingguo, College of Pharmacy, Liaoning University of

Table 1. NMR data of compound **1** (in CD_3OD).

Position	ΔC	δ_H
1	70.5	3.88 (1H, overlapped); 3.55 (1H, overlapped)
2	28.8	2.36 (2H, m)
3	125.9	5.39 (1H, dt, $J = 6.6$, 11.4 Hz)
4	134.4	5.43 (1H, dt, $J = 6.6$, 11.4 Hz)
5	21.5	2.07 (2H, m)
6	14.7	0.96 (3H, t, $J = 7.8$ Hz)
1′	103.1	4.40 (1H, d, $J = 7.8$ Hz)
2′	83.2	3.36 (1H, overlapped)
3′	77.7	3.54 (1H, overlapped)
4′	71.4	3.31 (1H, overlapped)
5′	77.9	3.25 (1H, m)
6′	62.6	3.66 (1H, overlapped); 3.86 (1H, overlapped)
1″	105.6	4.53 (1H, d, $J = 6.6$ Hz)
2″	73.1	3.64 (1H, overlapped)
3″	74.0	3.57 (1H, overlapped)
4″	69.2	3.81 (1H, overlapped)
5″	66.8	3.54 (1H, overlapped); 3.91 (1H, overlapped)

Traditional Chinese Medicine (TCM). A voucher specimen (no. yacon20050927) has been deposited at the Pharmacognosy Laboratory, College of Pharmacy, Liaoning University of TCM.

3.3. *Extraction and isolation*

The leaves of *S. sonchifolius* (6.0 kg) were extracted with water under reflux. Evaporation of the solvent under reduced pressure gave a condensed aqueous extract, which was then subjected to HPD-100 macroporous resin and eluted with water and 95% EtOH. The 95% EtOH elution was collected and the solvent was removed under reduced pressure to yield 150 g of residues. The extract was then subjected to normal-phase silica gel column and eluted with a gradient of $CHCl_3$–MeOH ($100:0 \rightarrow 0:100$, v/v) to give eight fractions. Fraction 4 ($CHCl_3$–MeOH, 70 : 30, v/v) was subjected to further separation using repeated ODS silica gel, Sephadex LH-20 column chromatography and HPLC to give compounds **1** (40 mg), **2** (80 mg) and **3** (100 mg).

3.3.1. *Z-hex-3-en-1-ol O-alpha-l-arabinopyransyl (1″-2′)-beta-d-glucopyranoside (**1**)*

White amorphous powder; $[\alpha]_D^{24}$ −58.1° (c 1.00, MeOH); positive ion ESI–MS: m/z 417 $[M + Na]^+$; high resolution (HR)-ESI–MS: Calcd for $C_{17}H_{30}O_{10}$ $[M + Na]^+$: 417.4039, Found: 417.4027; ^{1}H- and ^{13}C-NMR data in CD_3OD are shown in Table 1.

3.4. *Acid hydrolysis*

Solution of compound **1** in MeOH–HCl (1 : 1) was placed into a sealed capillary. After heating at 80°C for 4 h, the solution was subjected to silica gel thin layer

chromatography (TLC), together with the standard samples. *n*-BuOH–AcOH–H_2O and $CHCl_3$–MeOH–H_2O were used as the developing solvents and *O*-phthalic acid-aniline was used as the detection reagent. Glucose and arabinose were detected.

3.5. *Determination of sugar components*

Compound **1** (3 mg) in 10% HCl–dioxane (1 : 1, 1 mL) was heated at 80°C for 4 h. The reaction mixture was neutralised with Ag_2CO_3, filtered and then extracted with $CHCl_3$ (1 mL × 3). After concentration, monosaccharide subunits (H_2O layer) were obtained. The sugar residue was then dissolved in 2 mL of H_2O and analysed by HPLC under the following conditions described in the literature (Jiang, Qiu, Cheng, Kang, & Dou, 2008): column, Kaseisorb LC NH_2-60-5, 250 mm × 4.6 mm i.d. (Tokyo Kasei Kogyo Co. Ltd); solvent, MeCN–H_2O (3 : 1); flow rate, 0.8 mL min^{-1}; detection, optical rotation. Determination of D-glucose, L-arabinose present in the sugar fraction was carried out by comparison of its retention times and optical rotation with those of the standard sample.

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