# Three New *ent*-Kaurane Diterpenoids from *Siegesbeckia pubescens*

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Three new *ent*-kaurane glucopyranosides, 2-*O*-[*β*-D-apiofuranosyl-(1 → 3)-2-*O*-isovaleryl-*β*-D-glucopyranosyl]-4-*epi*-atractyligenin (**1**), 2-*O*-[*β*-D-apiofuranosyl-(1 → 3)-2-*O*-isovaleryl-*β*-D-glucopyranosyl]atractyligenin (**2**), and 2-*O*-[*β*-D-apiofuranosyl-(1 → 3)-2-*O*-(3-methylpentanoyl)-*β*-D-glucopyranosyl]-4-*epi*-atractyligenin (**3**), along with 2-*O*-(2-*O*-isovaleryl-*β*-D-glucopyranosyl)-4-*epi*-atractyligenin (**4**), were isolated for the first time from the aerial parts of *Siegesbeckia pubescens*. The structures were established by extensive spectroscopic analyses including 1D- and 2D-NMR (HSQC, HMBC, and ROESY), and HR-ESI-MS, and by comparison with published data.

**Introduction.** – Plants of the genus *Siegesbeckia* are annual herbs widely distributed in tropical, subtropical, and temperate parts of the world. Three species of this genus grow in China (*Siegesbeckia pubescens*, *S. orientalis*, and *S. glabrescens*), the aerial parts of which are being used as traditional Chinese medicines called 'Xi-Xian' to treat rheumatic arthritis, hypertension, malaria, and snake bite [1]. The chemical composition of the aerial part of *Siegesbeckia* has been investigated by several research groups [2–4].

The medicinal importance and diverse activities of members of this genus promoted us to undertake further phytochemical investigations of *Siegesbeckia pubescens*. In this article, we describe the isolation and structure elucidation of three new *ent*-kaurane glucopyranosides from the aerial parts of *Siegesbeckia pubescens*, namely 2-*O*-[*β*-D-apiofuranosyl-(1 → 3)-2-*O*-isovaleryl-*β*-D-glucopyranosyl]-4-*epi*-atractyligenin[1]) (**1**), 2-*O*-[*β*-D-apiofuranosyl-(1 → 3)-2-*O*-isovaleryl-*β*-D-glucopyranosyl]atractyligenin[1]) (**2**), and 2-*O*-[*β*-D-apiofuranosyl-(1 → 3)-2-*O*-(3-methylpentanoyl)-*β*-D-glucopyranosyl]-4-*epi*-atractyligenin[1]) (**3**), along with the known 2-*O*-(2-*O*-isovaleryl-*β*-D-glucopyranosyl)-4-*epi*-atractyligenin[1]) (**4**) isolated for the first time from this genus (*Fig. 1*).

**Results and Discussion**. – Repeated column chromatography (CC) of the EtOH extract from the the aerial parts of *Siegesbeckia pubescens* yielded compounds **1**–**4**.

Compound **1** was obtained as a yellow viscous oil. Its molecular formula was determined as $C_{35}H_{54}O_{14}$ from the HR-ESI-MS (*m*/*z* 721.3427 ($[M+Na]^+$). The $^{13}$C-NMR spectrum (*Table 1*) showed resonances of 35 C-atoms, which were classified

[1]) Trivial and arbitrary atom numbering; for systematic names, see *Exper. Part.*

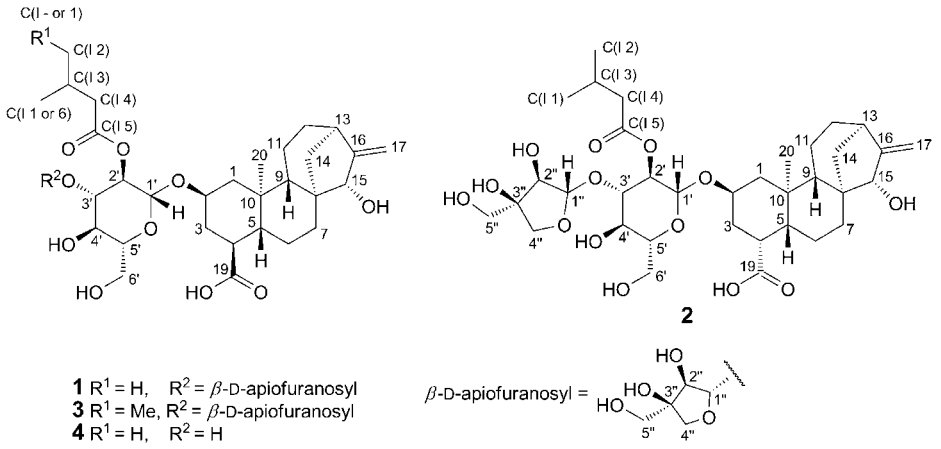


Fig. 1. *Compounds* **1**–**4**[1]) *isolated from* Siegesbeckia pubescens

by their chemical shifts, DEPT, and HSQC spectra as three Me groups, twelve $CH_2$ groups (three O-bearing and one olefinic), 14 CH groups (nine O-bearing), and six quaternary C-atoms (one olefinic, one COOH, and one ester C=O group). The $^1$H-NMR spectrum of **1** (*Table 1*) exhibited signals for one $\beta$-glucose unit and one $\beta$-apiose unit [5], comprising two anomeric H-atom signals at $\delta$(H) 4.63 (*d*, $J = 8.1$ Hz) and 5.01 (*d*, $J = 2.9$ Hz). Additionally, signals of an isovaleric acid (= 3-methylbutanoic acid) ester were observed at $\delta$(H) 2.32–2.24 (*m*, 2 H), 2.10 (*sept.*, $J = 6.8$ Hz, 1 H), 0.98 (*d*, $J = 2.0$ Hz, 3 H), and 0.98 (*d*, $J = 2.0$ Hz, 3 H). The presence of a $\beta$-glucose and a $\beta$-apiose unit was also evident by signals of the anomeric C-atoms at $\delta$(C) 100.9 and 111.6. The $^{13}$C-NMR signals of the sugar moieties were identified by a combination of the HMQC and HMBC data. The structure of the aglycon and position of the sugar and isovalerate moieties of **1** could be deduced from the 2D-NMR measurements, including the ROESY, HMQC, and HMBC experiments. The structure of the aglycon was shown to be a norditerpene by the presence of 19 signals in the $^{13}$C-NMR spectrum, in addition to the C-atom signals of the sugars and the isovalerate moieties. Moreover, the $^1$H-NMR spectrum showed only one Me signal, at $\delta$(H) 0.99, while the $^{13}$C-NMR spectrum showed one carboxylic C-atom signal at $\delta$(C) 178.8. Two O-bearing C-atoms found at $\delta$(C) 74.2 and 83.6 were correlated in the HMQC spectrum with the H-atom signals at $\delta$(H) 4.23 (*m*, H–C(2)) and 3.76 (br. *s*, H–C(15)), respectively. An olefinic group was detected by the signals at $\delta$(C) 160.4 and 109.0, and the corresponding H-atoms appeared at 5.18 and 5.07 (2 br. *s*, each 1 H). The positions of the functional groups and the sugar and isovalerate moieties were determined from the HMBC spectrum (*Fig. 2*). Thus, the C-atom at $\delta$(C) 74.2 (C(2)) showed a cross-peak with the anomeric H-atom at $\delta$(H) 4.63 (H–C(1′)) as well as with the H-atoms at $\delta$(H) 2.28 ($H_\alpha$–C(1)), 0.75 ($H_\beta$–C(1)), 2.38–2.42 ($H_\alpha$–C(3)), and 1.18–1.22 ($H_\beta$–C(3)), thereby furnishing the partial structure C(1)–C(2)(O-sugar)–C(3). This result was supported by the ROESY data (*Fig. 3*) which revealed the correlation of the anomeric H–C(1′) with $H_\alpha$–C(3) and H–C(2) ($\delta$(H) 4.20–4.25). The HMBC cross-peaks $\delta$(C) 173.6 (C(15))/$\delta$(H) 4.77 (H–C(2′)) and $\delta$(C) 84.2 (C(3′))/$\delta$(H) 5.01 (H–C(1″)) showed that

Table 1. *$^1$H- and $^{13}$C-NMR Data* ($CD_3OD$, 27°, 500 and 125 MHz resp) *of Compound* **1** *and* **2**. $\delta$ in ppm, $J$ in Hz.

| | **1** | | **2** | |
|---|---|---|---|---|
| | $\delta$(H) | $\delta$(C) | $\delta$(H) | $\delta$(C) |
| $CH_2$(1) | 2.28 (*dd*, $J$ = 2.0, 12.0, $H_\alpha$), 0.75 (*dd*, $J$ = 12.0, 12.0, $H_\beta$) | 48.9 | 2.28 (*dd*, $J$ = 2.0, 12.0, $H_\alpha$), 0.72 (*dd*, $J$ = 12.0, 12.0, $H_\beta$) | 48.9 |
| H–C(2) | 4.20–4.25 (*m*) | 74.2 | 4.28–4.35 (*m*) | 74.4 |
| $CH_2$(3) | 2.38–2.42 (*m*, $H_\alpha$), 1.18–1.22 (*td*, $J$ = 11.7, 6.7, $H_\beta$) | 35.7 | 2.39–2.43 (*m*, $H_\alpha$), 1.10–1.16 (*td*, $J$ = 12, 5.5, $H_\beta$) | 36.4 |
| H–C(4) | 2.66 (*td*, $J$ = 5.0, 1.7) | 44.7 | 2.57 (*td*, $J$ = 5.0, 1.6) | 46.0 |
| H–C(5) | 1.40 (br. *d*, $J$ = 5.4) | 50.4 | 1.37 (br. *d*, $J$ = 4.9) | 50.8 |
| $CH_2$(6) | 1.92 (*dd*, $J$ = 2.1, 13.2), 1.63–1.66 (*m*) | 26.6 | 1.95 (*dd*, $J$ = 2.5, 12.4), 1.66–1.68 (*m*) | 26.7 |
| $CH_2$(7) | 1.67–1.70, 1.42–1.48 (2 *m*) | 36.2 | 1.66–1.68, 1.39–1.42 (2 *m*) | 36.2 |
| H–C(8) | | 48.9 | | 48.9 |
| H–C(9) | 1.05 (br. *d*, $J$ = 6.3) | 54.5 | 1.02 (br. *d*, $J$ = 2.2) | 54.5 |
| C(10) | | 41.8 | | 41.8 |
| $CH_2$(11) | 1.42–1.48, 1.61–1.63 (2 *m*) | 19.2 | 1.39–1.50, 1.60–1.63 (2 *m*) | 19.2 |
| $CH_2$(12) | 1.42–1.48, 1.61–1.63 (2 *m*) | 33.6 | 1.39–1.50, 1.60–1.63 (2 *m*) | 33.6 |
| H–C(13) | 2.70 (br. *s*) | 43.7 | 2.69 (br. *s*) | 43.7 |
| $CH_2$(14) | 1.37 (br. *d*, $J$ = 10.0), 1.87 (br. *d*, $J$ = 11.6) | 37.2 | 1.32 (br. *d*, $J$ = 6.6), 1.95 (br. *d*, $J$ = 11.7) | 37.2 |
| H–C(15) | 3.76 (br. *s*) | 83.6 | 3.75 (br. *s*) | 83.6 |
| C(16) | | 160.4 | | 160.5 |
| $CH_2$(17) | 5.18, 5.07 (2 br. *s*) | 109.0 | 5.17, 5.06 (2 br. *s*) | 108.9 |
| C(18) | | 178.8 | | 180.6 |
| Me(20) | 0.99 (*s*) | 17.2 | 1.03 (*s*) | 17.4 |
| H–C(1′) | 4.63 (*d*, $J$ = 8.1) | 100.9 | 4.68 (*d*, $J$ = 8.1) | 100.7 |
| H–C(2′) | 4.77 (*dd*, $J$ = 8.1, 9.5) | 74.1 | 4.77 (*dd*, $J$ = 8.1, 9.5) | 74.1 |
| H–C(3′) | 3.62 (*dd*, $J$ = 8.8, 9.5) | 84.2 | 3.62 (*dd*, $J$ = 8.8, 9.5) | 84.2 |
| H–C(4′) | 3.44 (*dd*, $J$ = 8.8, 9.7) | 70.2 | 3.45 (*dd*, $J$ = 8.8, 9.7) | 70.2 |
| H–C(5′) | 3.34–3.37 (*m*) | 77.7 | 3.36–3.39 (*m*) | 77.5 |
| $CH_2$(6′) | 3.72 (*dd*, $J$ = 5.1, 12.0), 3.86 (*dd*, $J$ = 2.2, 12.0) | 62.5 | 3.72 (*dd*, $J$ = 5.0, 12.0), 3.85 (*dd*, $J$ = 2.4, 12.0) | 62.4 |
| H–C(1″) | 5.01 (*d*, $J$ = 2.9) | 111.6 | 5.02 (*d*, $J$ = 2.9) | 11.5 |
| H–C(2″) | 3.84 (*d*, $J$ = 2.9) | 78.0 | 3.84 (*d*, $J$ = 2.9) | 78.0 |
| C(3″) | | 80.4 | | 80.4 |
| $CH_2$(4″) | 4.10 (*d*, $J$ = 9.6), 3.78 (*d*, $J$ = 9.6) | 75.1 | 4.11 (*d*, $J$ = 9.8), 3.79 (*d*, $J$ = 9.8) | 75.1 |
| $CH_2$(5″) | 3.55 (*d*, $J$ = 1.5) | 65.2 | 3.56 (*d*, $J$ = 1.9) | 65.2 |
| Me(I 1) | 0.98 (*d*, $J$ = 2.0) | 22.9 | 0.99 (*d*, $J$ = 2.2) | 22.9 |
| Me(I 2) or $CH_2$(I 2) | 0.98 (*d*, $J$ = 2.0) | 22.9 | 0.98 (*d*, $J$ = 2.2) | 22.9 |
| H–C(I 3) | 2.10 (*sept.*, $J$ = 6.8) | 26.6 | 2.10 (*sept.*, $J$ = 6.8) | 26.6 |
| $CH_2$(I 4) | 2.32–2.24 (*m*) | 44.4 | 2.32–2.23 (*m*) | 44.4 |
| C(I 5) | | 173.6 | | 173.7 |

the isovalerate moiety was located at C(2′) and the $\beta$-apiose unit at C(3′).The Me signal at $\delta$(H) 0.99 showed a HMBC with $\delta$(C) 48.9 (C(1)), 50.4 (C(5)), and 52.9 (C(9)). The second C-bearing O-atom was placed at C(15) on the basis of the HMBC spectrum. In the ROESY experiment, $\delta$(H) 4.20–4.25 (H–C(2)) showed correlations with 2.28

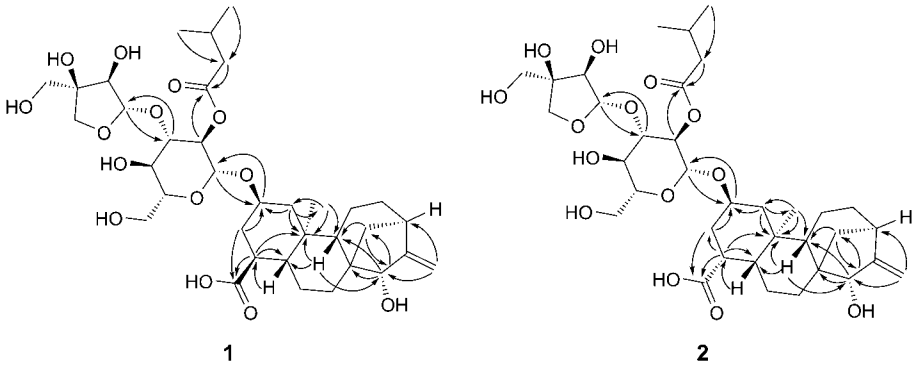

Fig. 2. *Key HMBCs of compounds* **1** *and* **2**

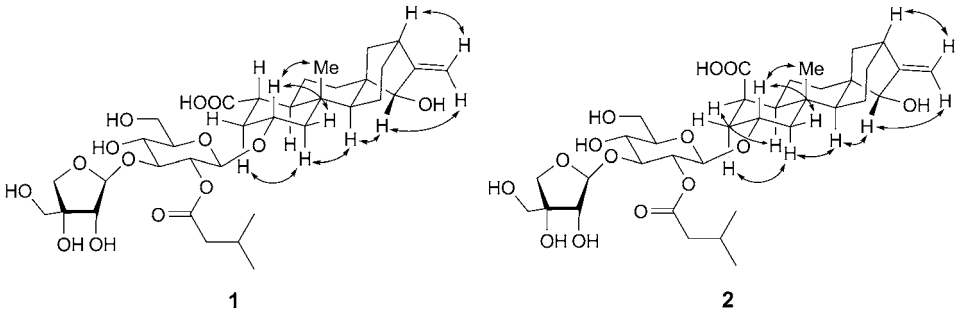

Fig. 3. *Key ROESY correlations of compounds* **1** *and* **2**

($H_\alpha$–C(1)) and 0.99 (*s*, Me(20)), but not with $\delta$(H) 1.40 (br. *d*, H–C(5)). Besides that, $\delta$(H) 0.75 ($H_\beta$–C(1)) showed correlations with $\delta$(H) 1.05 (H–C(9)), and the latter with $\delta$(H) 3.76 (H–C(15)). Finally, the structure and relative configuration of **1** were confirmed as 2-*O*-[$\beta$-D-apiofuranosyl-(1 → 3)-2-*O*-isovaleryl-$\beta$-D-glucopyranosyl]-4-*epi*-atractyligenin.

Compound **2** was obtained as a yellow powder. Its molecular formula was determined as $C_{35}H_{54}O_{14}$ from the HR-ESI-MS (*m*/*z* 721.3433 ([*M* + Na]$^+$). The $^1$H- and $^{13}$C-NMR data of **2** (*Table 1*) suggested that its structure is similar to that of compound **1**, except for C(4) and H–C(4) and others which have relations with C(4) and H–C(4). The ROESY experiment indicated a correlation between H–C(4) and H–C(5) (*Fig. 3*), which confirmed the $\beta$-configuration of COOH group at C(4) in **2**. Consequently, the structure of compound **2** was established as the 2-*O*-[$\beta$-D-apiofuranosyl-(1 → 3)-2-*O*-isovaleryl-$\beta$-D-glucopyranosyl]atractyligenin.

Compound **3** was obtained as a white powder. The relative molecular mass of **3** was determined as 712 on the basis of the ion peak *m*/*z* 711 ([*M* − H]$^+$) in the ESI-MS. The structure of **3** was found to be similar to that of **1**, except for the molecular mass (**3** = **1** + 14). The $^1$H- and $^{13}$C-NMR data of **3** and **1** were almost coincident with respect to their $\beta$-glucose and $\beta$-apiose units and the aglycon (*Table 2*). The $^1$H-NMR spectrum showed an additional Me group in the ester side chain. Closer inspection revealed that

Table 2. *$^1$H- and $^{13}$C-NMR Data* ($CD_3OD$, 27°, 500 and 125 MHz, resp.) *of Compound* **3**. $\delta$ in ppm, $J$ in Hz.

| | $\delta$(H) | $\delta$(C) | | $\delta$(H) | $\delta$(C) |
|---|---|---|---|---|---|
| $CH_2$(1) | 2.28 (*dd*, $J$ = 3.7, 12.0, $H_\alpha$), | 48.9 | H–C(1′) | 4.63 (*d*, $J$ = 8.1) | 100.8 |
| | 0.75 (*dd*, $J$ = 12.0,12.0, $H_\beta$) | | H–C(2′) | 4.77 (*dd*, $J$ = 8.1, 9.5) | 74.1 |
| H–C(2) | 4.22–4.27 (*m*) | 74.1 | H–C(3′) | 3.62 (*dd*, $J$ = 8.8, 9.5) | 84.2 |
| $CH_2$(3) | 2.38–2.42 (*m*, $H_\alpha$), | 35.8 | H–C(4′) | 3.44 (*dd*, $J$ = 8.8, 9.7) | 70.3 |
| | 1.20 (*td*, $J$ = 11.7, 6.7, $H_\beta$) | | H–C(5′) | 3.34–3.37 (*m*) | 77.7 |
| H–C(4) | 2.66 (*td*, $J$ = 5.0, 1.7) | 44.8 | $CH_2$(6′) | 3.72 (*dd*, $J$ = 5.1, 12.0), | 62.5 |
| H–C(5) | 1.40 (br. *d*, $J$ = 5.3) | 50.5 | | 3.86 (*dd*, $J$ = 2.2, 12.0) | |
| $CH_2$(6) | 1.93 (*dd*, $J$ = 2.1, 13.2), | 26.6 | H–C(1″) | 5.01 (*d*, $J$ = 2.8) | 111.6 |
| | 1.63–1.66 (*m*) | | H–C(2″) | 3.84 (*d*, $J$ = 2.8) | 78.0 |
| $CH_2$(7) | 1.67–1.70 (*m*), 1.42–1.48 (*m*) | 36.2 | C(3″) | | 80.4 |
| C(8) | | 48.9 | $CH_2$(4″) | 4.10 (*d*, $J$ = 9.6), 3.78 (*d*, $J$ = 9.6) | 75.1 |
| H–C(9) | 1.05 (br. *d*, $J$ = 7.2) | 54.5 | $CH_2$(5″) | 3.55 (*d*, $J$ = 1.5) | 65.2 |
| C(10) | | 41.8 | Me(I 1) | 0.92 (*t*, $J$ = 7.5) | 11.7 |
| $CH_2$(11) | 1.42–1.48 (*m*), 1.61–1.63 (*m*) | 19.2 | $CH_2$(I 2) | 1.37–1.47 (*m*), 1.17–1.30 (*m*) | 30.4 |
| $CH_2$(12) | 1.42–1.48 (*m*), 1.61–1.63 (*m*) | 33.6 | H–C(I 3) | 1.86–1.94 (*m*) | 33.0 |
| H–C(13) | 2.71(br. *s*) | 43.7 | $CH_2$(I 4) | 2.40 (*dd*, $J$ = 6.3, 15.2), | 42.5 |
| $CH_2$(14) | 1.38 (br. *d*, $J$ = 5.2), | 37.2 | | 2.21 (*dd*, $J$ = 7.8, 15.2) | |
| | 1.87 (br. *d*, $J$ = 12.9) | | C(I 5) | | 173.8 |
| H–C(15) | 3.76 (br. *s*) | 83.6 | Me(I 6) | 0.97 (*d*, $J$ = 8.6) | 19.8 |
| C(16) | | 160.4 | | | |
| $CH_2$(17) | 5.18 (br. *s*), 5.07 (br. *s*) | 109.0 | | | |
| C(18) | | 180.0 | | | |
| Me(20) | 1.00 (*s*) | 17.2 | | | |

the former isopropyl group was replaced by the $CH_2$ homologous (1-methyl)propyl unit in **3**. The $^{13}$C-NMR spectrum, with $\delta$(C) 11.7, 30.4, 33.0, 42.5, 173.8, and 19.8, showed that the different unit connected with C(2′) was 3-methylpentanoate [6]. The structure of **3** was established as the 2-*O*-[$\beta$-D-apiofuranosyl-(1 → 3)-2-*O*-(3-methylpentanoyl)-$\beta$-D-glucopyranosyl]-4-*epi*-atractyligenin.

The known compound **4** was isolated for the first time from this genus. The structure of compound **4** was assigned by its spectral data and comparison with those reported in the literature [7].

## Experimental Part

*General.* Column chromatography (CC): silica gel ($SiO_2$, 200–300 mesh; *Qingdao Marine Chemical Plant*), *Sephadex LH-20* (*GE Healthcare Bio-Sciences AB*, USA), and *MCI* gel (*Mitsubishi Chemical Corporation*, Tokyo, Japan). TLC: silica gel $GF_{254}$ (10–40 μm; *Qingdao Marine Chemical Plant*, Qingdao, P. R. China). $^1$H-, $^{13}$C-, and 2D-NMR Spectra: *Bruker-AV-500* spectrometers; $\delta$ in ppm rel. to $Me_4Si$ as internal standard, $J$ in Hz. ESI-MS: *Agilent 1100 JC/MSD Trap* spectrometer; in $m/z$. HR-ESI-MS: *Micro Q-TOF* spectrometer; in $m/z$.

*Plant Material.* The aerial parts of *Siegesbeckia pubescens* were purchased from *Bozhou Bohua Pharmaceutical Co., Ltd.*, Anhui Province, P. R. China (December 2009), and identified by *M.-J. Qin*, the curator of China Pharmaceutical University (China). A voucher specimen has been deposited with the Department of Natural Medicinal Chemistry, China Pharmaceutical University, Nanjing, P. R. China.

*Extraction and Isolation*. The air-dried and powdered *Siegesbeckia pubescens* (10 kg) was extracted with 95% EtOH. The crude extract was mixed with $H_2O$ (5 l) to form a suspension and then extracted successively with petroleum ether, AcOEt, and BuOH. The AcOEt-soluble part (130 g) was subjected to CC (*MCI*, EtOH/$H_2O$ 1:10, 4:6, 3:1, and 10:1): *Fractions A – D. Fr. B* was separated by CC (*ODS* acetone/$H_2O$ 1:2 and 1:1). Each subfraction of *Fr. B* was subjected to repeated CC ($SiO_2$, *Sephadex LH-20* CC), and further purified by recrystallization. At last, compounds **1** (60 mg), **2** (10 mg), **3** (6 mg), and **4** (20 mg) were isolated.

*2*-O-*[β*-D-*Apiofuranosyl-(1 → 3)-2*-O-*isovaleryl-β*-D-*glucopyranosyl]-4*-epi-*atractyligenin* (= *(2β,4β,15α)-2-{[3*-O-*β*-D-*Apiofuranosyl-2*-O-*(3-methyl-1-oxobutyl)-β*-D-*glucopyranosyl]oxy}-15-hydroxy-19-nor*-ent-*kaur-16-en-18-oic Acid*; **1**). Yellow, viscous oil. $^1$H- and $^{13}$C-NMR: *Table 1*. HR-ESI-MS: 721.3427 ($[M+Na]^+$; calc. 721.3411).

*2*-O-*[β*-D-*Apiofuranosyl-(1 → 3)-2*-O-*isovaleryl-β*-D-*glucopyranosyl]atractyligenin* (= *(2β,4α,15α)-2-{[3*-O-*β*-D-*Apiofuranosyl-2*-O-*(3-methyl-1-oxobutyl)-β*-D-*glucopyranosyl]oxy}-15-hydroxy-19-nor*-ent-*kaur-16-en-18-oic Acid*; **2**). Yellow powder. $^1$H- and $^{13}$C-NMR: *Table 1*. HR-ESI-MS: 721.3433 ($[M+Na]^+$, calc. 721.3411).

*2*-O-*[β*-D-*Apiofuranosyl-(1 → 3)-2*-O-*(3-methylpentanal)-β*-D-*glucopyranosyl]-4*-epi-*atractyligenin* (= *(2β,4β,15α)-2-{[3*-O-*β*-D-*Apiofuranosyl-2*-O-*(3-methyl-1-oxopentyl)-β*-D-*glucopyranosyl]oxy}-15-hydroxy-19-nor*-ent-*kaur-16-en-18-oic Acid*; **3**). White powder. $^1$H- and $^{13}$C-NMR: Table 2. ESI-MS: 711 ($[M-H]^+$).

*2*-O-*[2*-O-*Isovaleryl-β*-D-*glucopyranosyl]-4*-epi-*atractyligenin* (= *(2β,4β,15α)-15-Hydroxy-2-{[2*-O-*(3-methyl-1-oxobutyl)-β*-D-*glucopyranosyl]oxy}-19-nor*-ent-*kaur-16-en-18-oic Acid*; **4**). Yellow oil. $^1$H-NMR (500 MHz, $CD_3OD$): 5.18 (br. *s*, $H_a$–C(17)); 5.07 (br. *s*, $H_b$–C(17)); 4.68 (*dd*, *J* = 8.1, 9.5, H–C(2′)); 4.59 (*d*, *J* = 8.1, H–C(1′)); 4.22 (*m*, H–C(2)); 3.86 (*dd*, *J* = 2.4, 12.0, $H_b$–C(6)); 3.76 (br. *s*, H–C(15)); 3.70 (*dd*, *J* = 5.3, 12.0, $H_a$–C(17)); 3.50 (*t*, *J* = 6.0, H–C(4′)); 3.38 (*m*, H–C(5′)); 2.71 (br. *s*, H–C(13)); 2.66 (*td*, *J* = 5.0, 1.7, H–C(4)); 2.26 – 2.24 (*m*, H–C(I 4)); 2.10 (*sept.*, *J* = 6.8, H–C(I 3)); 1.05 (br. *d*, *J* = 6.3, H–C(9)); 0.99 (*s*, Me(20)); 0.98 (*d*, *J* = 2.0, Me(I 1)); 0.98 (*d*, *J* = 2.0, Me(I 2)). $^{13}$C-NMR (125 MHz, $CD_3OD$): 178.8 (C(18)); 173.8 (C(I 5)); 160.3 (C(16)); 109.0 (C(17)); 101.1 (C(1′)); 83.5 (C(15)); 77.9 (C(5′)); 76.3 (C(2′)); 75.1 (C(3′)); 74.1 (C(2)); 71.7 (C(4′)); 62.6 (C(6′)); 54.4 (C(9)); 50.4 (C(5)); 48.8 (C(1)); 48.8 (C(8)); 44.6 (C(4)); 44.4 (C(I 4)); 43.7 (C(13)); 41.8 (C(10)); 37.2 (C(14)); 36.1 (C(7)); 35.6 (C(3)); 33.6 (C(12)); 26.8 (C(6)); 26.6 (C(I 3)); 22.9 (C(I 1)); 22.8 (C(I 2)); 19.2 (C(11)); 17.2 (C(20)). ESI-MS: 565 ($[M-H]^+$).

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