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Anti-complement Activity of Triterpenoids from the Whole Plant of *Patrinia saniculaefolia*

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Abstract – Two oleanane-type triterpenes (**1**, **2**) and their glycosides (**4** - **6**), and one ursane-type triterpene (**3**) have been isolated from a methanolic extract of *Patrinia saniculaefolia* Hemsley (Valerianaceae) through repeated silica gel and reversed-phase C-18 column chromatography. Their chemical structures were determined as oleanolic acid (**1**), oleanonic acid (**2**), 23-hydroxyursolic acid (**3**), 3-*O*-α-L-arabinopyranosyl-oleanolic acid (**4**), 3-*O*-β-D-glucopyranosyl-oleanolic acid (**5**), and oleanolic acid 3-*O*-[α-D-xylopyranosyl-(1 → 3)-β-D-glucuronopyranoside-6-*O*-butyl-ester] (**6**) on the basis of their MS, ^{1}H-, and ^{13}C-NMR spectral data. All compounds were isolated from the whole plant of the *P. saniculaefolia* for the first time. These compounds were examined for their anti-complement activity against the classical pathway of the complement system. Among them, compounds **1** - **3** exhibited anti-complement activity with IC_{50} values of 470.1, 212.2, and 121.0 μM, respectively, whereas compounds **4** - **6** were inactive. These results suggest that the carbonyl or hydroxy group at C-3 in the oleanane- and/or ursane-triterpenes are important for the anti-complement activity against the classical pathway.
Keywords – *Patrinia saniculaefolia*, Valerianaceae, 23-hydroxyursolic acid, anti-complement activity

Introduction

In our collaborative program to search for novel anti-complement agents from the Plant Kingdom, a methanol extract of the whole plant of *Patrinia saniculaefolia* Hemsley (Valerianaceae) showed promising bioactivity, as evaluated against the classical pathway of the complement system. *P. saniculaefolia* is a perennial herb and an endemic species in Korea. The genus *Patrinia* is taxonomically classified into four species, *P. saniculaefolia*, *P. scabiosaefolia*, *P. villosa*, and *P. rupestris* (Lee, 1980; Lee, 1996). This genus is one of the valuable crude drugs which has been used in Korea and China as a traditional folk medicine for the treatment of initial stages of edema, appendicitis, endometriosis and inflammation. Saponins, coumarins, iridoids, and flavonoids isolated from this genus have demonstrated sedative, antibacterial, and cytotoxic effects (Bae, 2000; Li *et al*., 2001). We have reported the three iridoids isolated from the whole of this plant, two of which are new, namely, patridoids I and II, and the other one, nardostatin, a known iridoid. (An *et al*., 2003). These compounds were shown to display anti-inflammation (Ju *et al*., 2003a; Ju *et al*., 2003b).

In this work, we further report the isolation and structure determination of ursane- and oleanane-type triterpenes, and the glycosides, which were firstly isolated from the *P. saniculaefolia*, and the anti-complement activity using the classical pathway of complement system.

Experimental

General experimental procedures – Melting points were measured by an electrothermal melting apparatus and are uncorrected. UV spectra were recorded on a Milton Roy Spectronic 3000 spectrophotometer. IR spectra were determined on an IR Report-100 spectrophotometer (JASCO). FAB-MS spectra were measured on an Autospec Mass spectrometer (Micromass). NMR spectra were recorded on a Bruker NMR DRX300, 600 spectrometer, with the chemical shift being represented in parts per million (ppm, δ) with tetramethylsilane (TMS) as an internal standard. Column chromatography was

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carried out on silica-gel 70 - 230 and 230 - 400 mesh (Merck). Thin layer chromatography (TLC) was performed on precoated silica gel 60 GF_{254} (Merck) and RP-$18F_{254S}$ (Merck) plates, and spots were detected by spraying with 10% H_2SO_4.

Plant Material – The whole plant of *P. saniculaefolia* was collected during August 1999 at Mt. Chiri, Jeonnam Province, Korea, and identified by Professor KiHwan Bae of the College of Pharmacy, Chungnam National University, Korea. A voucher specimen (CNU 2017) has been deposited in the herbarium of the College of Pharmacy, Chungnam National University, Korea.

Extraction and isolation – The dried whole plant (1.5 kg) of *P. saniculaefolia* was extracted three times with MeOH (2 L) at room temperature for 3 days. The combined MeOH extracts were concentrated under reduced pressure and obtained the MeOH extract (150.0 g). The extract was suspended in H_2O (1.5 L) and then fractionated sequentially with hexane, methylene chloride (CH_2Cl_2) and water-saturated butanol (BuOH), 3 times with each solvent. Removal of the solvents afforded 19.0 g, 16.0 g and 35.0 g of the hexane, CH_2Cl_2 and BuOH fractions, respectively. The hexane fraction (19.0 g) was subjected to column chromatography over silica gel eluted with a gradient of hexane and acetone to afford three fractions (Fr. 1 - 3). Fraction 3 was rechromatographed on a silica gel column and eluted with hexane-acetone (10 : 1) to give compounds **1** (85.7 mg), and **2** (52.0 mg). The CH_2Cl_2 fraction (16.0 g) was fractionated into three subfractions (Fr. 1 - 3) by a silica gel column chromatography and eluted with a gradient of CH_2Cl_2 and MeOH. Fraction 1 was also rechromatographed on a silica gel column eluted with a gradient of CH_2Cl_2 and MeOH and afforded compounds **3** (20.2 mg), and **4** (16.3 mg). The BuOH fraction (35.0 g) was chromatographed on silica gel column using CH_2Cl_2-MeOH and CH_2Cl_2-MeOH-H_2O step gradient system to give two fractions (Fr. 1 and 2). Fraction 1 was repeated column chromatography on silica gel ($CHCl_3$-MeOH-H_2O, 70 : 30 : 2) and RP-C_{18} column chromatography (60% aq. MeOH) afforded compound **5** (49.0 mg). Fraction 2 was chromatographed on a RP-C_{18} column eluted with MeOH-H_2O (60 : 40) to give compound **6** (34.0 mg).

Oleanolic acid (**1**): Colourless needles (MeOH); mp: 300 - 302 °C; $[\alpha]_D$: +64.6° (*c* 0.27, $CHCl_3$); UV (MeOH) λmax (log ε): 220 (2.83) nm; FABMS *m/z*: 479.2 $[M + Na]^+$; IR (KBr) ν_{max} cm^{-1}: 3400 (OH), 1680 (COOH), 1630 (C = C), 825 (trisubstitued double bond); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.76 (3H, s, H-26), 0.78 (3H, s, H-24), 0.91 (3H, s, H-29), 0.92 (3H, s, H-25), 0.94 (3H, s, H-30), 0.99 (3H, s, H-23), 1.14 (3H, s, H-27), 2.83 (1H, dd, *J* = 4.1, 13.5 Hz, H-18), 3.22 (1H, dd, *J* = 4.1, 11.3 Hz, H-3α), 5.29 (1H, t, *J* = 3.5 Hz, H-12); ^{13}C-NMR data: see Table 1.

Oleanonic acid (**2**): Colourless needles (MeOH); mp: 226 - 229 °C; $[\alpha]_D$: +101° (*c* 1.63, $CHCl_3$); UV (MeOH) λmax (log ε): 220 (2.83) nm; FABMS *m/z*: 477.2 $[M + Na]^+$; IR (KBr) ν_{max} cm^{-1}: 3400 (OH), 1735 (COOH), 1700 (C = O); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81 (3H, s, H-26), 0.91 (3H, s, H-29), 0.93 (3H, s, H-30), 1.03 (3H, s, H-24), 1.05 (3H, s, H-25), 1.08 (3H, s, H-23), 1.14 (3H, s, H-27), 2.37 and 2.55 (each 1H, m, H-2), 2.84 (1H, dd, *J* = 4.1, 13.7 Hz, H-18), 5.30 (1H, t, *J* = 3.4 Hz, H-12); ^{13}C-NMR data: see Table 1.

23-hydroxyursolic acid (**3**): White amorphous powder; mp: 283 - 285 °C; $[\alpha]_D$: +64.0° (*c* 0.27, MeOH); UV (MeOH) max (log ε): 280 (2.05), 204 (3.60) nm; FABMS *m/z*: 495.3 $[M + Na]^+$; IR (KBr) ν_{max} cm^{-1}: 3400 (OH), 1700 (COOH); ^{1}H NMR (600 MHz, pyridine-d_5) δ: 0.94 (3H, d, *J* = 6.5 Hz, H-30), 0.98 (3H, s, H-25), 1.00 (3H, d, *J* = 6.4 Hz, H-29), 1.01 (3H, s, H-26), 1.06 (3H, s, H-24), 1.19 (3H, s, H-27), 2.64 (1H, d, *J* = 11.2 Hz, H-18), 3.72 (1H, d, *J* = 10.4 Hz, H-23a), 4.18 (1H, d, *J* = 10.4 Hz, H-23b), 4.21 (1H, dd, *J* = 4.9, 11.4 Hz, H-3), 5.49 (1H, br. s, H-12); ^{13}C-NMR data: see Table 1.

3-*O*-α-L-arabinopyranosyl-oleanolic acid (**4**): Colourless needles (MeOH); mp: 249 - 252 °C; $[\alpha]_D$: +53.1° (*c* 2.0, MeOH); UV (MeOH) λmax (log ε): 232 (3.9) nm; FABMS *m/z*: 611.51 $[M + Na]^+$; IR (KBr) ν_{max} cm^{-1}: 3200 (OH), 1730 (COOH), 1650; ^{1}H NMR (600 MHz, pyridine-d_5) δ: 0.86 (3H, s, H-25), 0.96 (3H, s, H-24), 0.97 (3H, s, H-29), 1.01 (3H, s, H-26), 1.02 (3H, s, H-30), 1.29 (3H, s, H-23), 1.31 (3H, s, H-27), 3.31 (1H, dd, *J* = 3.9, 13.7 Hz, H-18), 3.36 (1H, dd, *J* = 4.1, 11.5 Hz, H-3), 3.85 (1H, d, *J* = 11.4 Hz, Ara H-5a), 4.18 (1H, dd, *J* = 3.0, 8.7 Hz, Ara H-3), 4.33 (2H, m, Ara H-4 and H-5b), 4.44 (1H, t, *J* = 7.9 Hz, Ara H-2), 4.78 (1H, d, *J* = 7.0 Hz, Ara H-1), 5.49 (1H, br. s, H-12); ^{13}C-NMR data: see Table 1.

3-*O*-β-D-glucopyranosyl-oleanolic acid (**5**): White amorphous powder; mp: 227 - 229 °C; $[\alpha]_D$: +46.9° (*c* 1.0 MeOH); FABMS *m/z*: 619 $[M + H]^+$; IR (KBr) ν_{max} cm^{-1}: 3400, 1690, 1075, 1025; ^{1}H NMR (600 MHz, pyridine-d_5) δ: 0.82 (3H, s, H-25), 0.95 (3H, s, H-24), 0.95 (3H, s, H-29), 0.98 (3H, s, H-26), 1.00 (3H, s, H-30), 1.30 (3H, s, H-23), 1.30 (3H, s, H-27), 3.29 (1H, dd, *J* = 3.8, 13.8 Hz, H-18), 3.38 (1H, dd, *J* = 4.3, 11.7 Hz, H-3), 4.11 (1H, t, *J* = 6.1 Hz, Glc H-5), 4.16 (1H, dd, *J* = 3.3, 9.4 Hz, Glc H-3), 4.43-4.49 (2H, m, Glc H-2 and Glc H-6), 4.58 (1H, d, *J* = 3.0 Hz, Glc H-4), 4.85 (1H, d, *J* = 7.7Hz, Glc H-1), 5.47(1H, t-like, H-12); ^{13}C-NMR data: see Table 1.

Table 1. ^{13}C-NMR spectral data of compounds **1 - 6**

position	**1**	**2**	**3**	**4**	**5**	**6**
1	38.4	39.1	39.0	38.8	38.7	38.6
2	27.2	34.0	27.7	26.7	26.6	26.6
3	79.0	217.8	73.5	88.7	88.7	89.3
4	38.7	47.4	42.9	39.6	39.5	39.5
5	55.2	55.3	48.6	55.9	55.8	55.7
6	18.3	19.5	18.6	18.5	18.5	18.4
7	32.6	32.1	33.3	33.3	33.3	33.2
8	39.2	39.2	40.0	39.8	39.7	39.7
9	47.6	46.8	48.1	48.1	48.0	48.0
10	37.1	36.8	37.2	37.0	37.0	36.9
11	22.9	23.4	23.7	23.7	23.7	23.7
12	122.6	122.3	125.5	122.5	122.5	122.5
13	143.6	143.6	139.4	144.8	144.8	144.8
14	41.6	41.7	42.6	42.2	42.2	42.1
15	27.7	27.6	28.8	28.2	28.3	28.3
16	23.4	22.8	25.0	23.8	23.7	23.7
17	46.5	46.5	48.1	46.7	46.6	46.6
18	40.9	41.0	53.6	42.1	42.0	42.0
19	45.8	45.8	39.6	46.5	46.5	46.4
20	30.7	30.6	39.5	31.0	31.0	30.9
21	33.8	33.8	31.2	34.2	34.2	34.2
22	33.1	32.4	37.5	33.2	33.2	33.2
23	28.1	26.4	67.9	28.2	28.2	28.0
24	15.5	21.4	13.2	16.9	17.0	16.9
25	15.3	15.0	16.2	15.5	15.5	15.4
26	17.1	17.0	17.6	17.4	17.4	17.3
27	25.9	25.8	23.9	26.2	26.2	26.1
28	183.1	184.1	180.7	180.2	180.1	180.1
29	32.4	33.0	17.6	33.3	33.2	33.3
30	23.6	23.5	21.4	23.8	23.7	23.7
butyl						65.0
						30.8
						19.2
						13.7
sugar moieties				arabinose	glucose	GlcA
1				107.5	107.5	106.9
2				73.0	73.2	74.5
3				74.7	76.8	86.2
4				69.6	70.3	71.1
5				66.8	75.5	76.8
6					62.4	170.0
						Xyl
1						106.3
2						75.4
3						78.2
4						70.9
5						67.3

Oleanolic acid 3-*O*-[*β*-D-xylopyranosyl-(1 → 3)-*β*-D-glucuronopyranoside-6-*O*-butyl-ester] (**6**): white amorphous powder; mp: 200 - 202 °C; HRFABMS *m/z*: 843.4871 $[M + Na]^+$; IR (KBr) ν_{max} cm^{-1}: 3400, 1740, 1700; ^{1}H NMR (600 MHz, pyridine-d_5) δ: 0.79 (3H, t, *J* = 7.4 Hz, GlcA-butyl ester, CH_3), 0.82, 0.97, 0.97, 1.00, 1.02, 1.30, 1.33 (each 3H, s, CH_3), 3.31 (1H, dd, *J* = 4.2, 14.0 Hz, H-18), 3.35 (1H, dd, *J* = 4.2, 12.0 Hz, H-3), 3.72 (1H, t, *J* = 10.4 Hz, xyl Ha-5), 4.16 (3H, m, GlcA H-2, xyl H-2 and xyl H-4), 4.29 (2H, m, GlcA-butyl ester, COOCH_2-), 4.34 (2H, m, GlcA H-3 and xyl Hb-5), 4.43 (1H, t, *J* = 9.4 Hz, GlcA H-4), 4.60 (1H, d, *J* = 9.7 Hz, GlcA H-5), 5.00 (1H, d, *J* = 7.8 Hz, GlcA H-1), 5.36 (1H, d, *J* = 7.6 Hz, xyl H-1), 5.47 (1H, br. s, H-12); ^{13}C-NMR data: see Table 1.

Anti-complement Assay – The *in vitro* anti-complement activity of the isolated compounds was examined according to a previously described method (Min *et al.*, 2004). For the classical pathway assay, a diluted solution of normal human serum (80 μL) collected from a healthy male volunteer was mixed with gelatin veronal buffer

($GVB2^+$, 80 μL) with or without tested sample. Each sample was dissolved in DMSO, and used as a negative control. The mixture was pre-incubated at 37 °C for 30 min and then 40 μL of sensitized erythrocytes (sheep red blood cells) were added. After incubation under the same conditions, the mixture was centrifuged at 1500 rpm and 4 °C for 10 min. The optical density of the supernatant (100 μL) was measured at 405 nm. Tiliroside was employed as positive control (Jung *et al*., 1998).

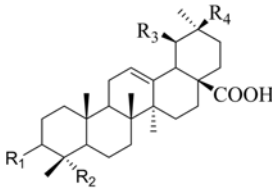
Results and Discussion

The hexane-, CH_2Cl_2-and BuOH-soluble fractions of the MeOH extract from the whole plant of *P. saniculaefolia* was subjected to silica gel and reversed-phase C-18 column chromatography to obtain six compounds (**1** - **6**). The isolated compounds were identified as oleanolic acid (**1**) (Do *et al*., 1991), oleanonic acid (**2**) (Seo *et al*., 1975; Tursch *et al*., 1967), 3-*O*-α-L-arabinopyranosyl-oleanolic acid (**4**) (Kitanaka *et al*., 1995), and 3-*O*-*β*-D-glucopyranosyl-oleanolic acid (**5**) (Abdel-Kader *et al*., 2000).

Compound **3** was obtained as white amorphous powder, mp 283 - 285 °C, and its molecular formula of $C_{30}H_{48}O_4$ was determined by the FABMS (*m/z* 495.3 [M + Na]$^+$). Its IR spectrum exhibited broad vibaration bands at 3400 cm^{-1} (hydroxy groups) and 1700 cm^{-1} (acid group). The ^{1}H NMR spectrum of **3** showed six methyl signals at δ 0.94 (3H, d, *J* = 6.5 Hz), 0.98 (3H, s), 1.00 (3H, d, *J* = 6.4 Hz), 1.01 (3H, s), 1.06 (3H, s), and 1.19 (3H, s). In addition, the doublet at δ 2.64 (1H, d, *J* = 11.2 Hz) and the olefinic proton at δ 5.49 (1H, br. s) were exhibited. From these spectral data, it is suggested that **3** is to be the urs-12-ene-28-oic acid skeleton. The doublet of doublets at δ 4.21 (1H, dd, *J* = 4.9, 11.4 Hz), 3.72 (1H, d, *J* = 10.4 Hz), and 4.18 (1H, d, *J* = 10.4 Hz) supposed that the two hydroxyl groups exist at the C-3*β* and C-23 positions. The ^{13}C-NMR spectrum also suggested the trihydroxylated ursenoic acid structure with the presence one carboxyl carbon signals at δ 180.7 (C-28), two olefinic carbon signals at δ 125.5 (C-12) and 139.4 (C-13), and two hydroxylated carbons at δ 73.5 (C-3) and 67.9 (C-23). The identity of **3** as 23-hydroxyursolic acid (3*β*, 23-dihydroxyurs-12-en-28-oic acid) was confirmed by comparison of reported spectral data (Li *et al*., 1995).

Compound **6** was obtained as a colorless powder, mp 200 - 202 °C, and its molecular formula of $C_{45}H_{72}O_{13}$ was determined from the [M + Na]$^+$ ion at *m/z* 843.4871 in the HRFABMS and from its ^{13}C and DEPT NMR spectral data. The IR spectrum exhibited absorptions at 3400 cm^{-1} (hydroxy group), 1700 and 1740 cm^{-1} (ester carbonyl groups). The seven tertiary methyl groups (δ 0.82, 0.97, 0.97, 1.00, 1.02, 1.30, and 1.33) and one trisubstituted olefinic proton (δ 5.47, br. s) observed in the ^{1}H NMR spectrum coupled with the information from the ^{13}C NMR spectrum (seven sp^3 carbons at δ 15.4, 16.9, 17.3, 23.7, 26.1, 28.0, and 33.3 and two sp^2 olefinic carbons at δ 122.5 and 144.8) indicated that the aglycon possesses an olean-12-ene skeleton. After an extensive 2D NMR study, the aglycon was identified as oleanolic acid. The ^{1}H and ^{13}C NMR spectra of **6** exhibited two sugar anomeric protons at δ 5.00 (1H, d, *J* = 7.8 Hz), and 5.36 (1H, d, *J* = 7.6 Hz) and anomeric carbons at δ 106.9 and 106.3. The HMBC and TOCSY spectra allowed immediate identification of two sugars as glucuronic acid and xylose. Vicinal coupling constants in these sugars were larger than 7.0 Hz indicating axial positions for protons in the *β*-linkages. The linkage of the sugar units at C-3 was established from the HMBC correlations of H-1 (δ 5.36) of xylose with C-3 (δ 86.2) of glucuronic acid, and the long-ranged HMBC correlation between H-1 (δ 5.00) of glucuronic acid and C-3 (δ 89.3) of the aglycon. Of the 45 carbons signals observed in the ^{13}C NMR spectrum of **6**, 30 carbons were assigned to the aglycon part, and the remaining 15 carbons to the disaccharide and an alkyl moiety at glucuronic acid. The presence of a butyl group was confirmed by ^{13}C NMR analysis which revealed four carbon signals at δ 13.7, 19.2, 30.8 and 65.0. In addition, the ^{1}H NMR spectrum contained a multiplet at δ 4.29 attributed to OCH_2 of the butyl chain and a methyl triplet at δ 0.79. All the above evidence led to the identification of compound **6** as oleanolic acid 3-*O*-[*β*-D-xylopyranosyl-(1 → 3)-*β*-D-glucuronopyranoside-6-*O*-butyl-ester] (Kawamura *et al*., 1988).

The compounds **1** - **6** isolated from *P. saniculaefolia* were tested for their anti-complement activity and the



	R_1	R_2	R_3	R_4
1	OH	H	H	CH_3
2	-O-	H	H	CH_3
3	OH	CH_2OH	CH_3	H
4	Ara	H	H	CH_3
5	Glc	H	H	CH_3
6	Xyl-(1-3)-6-*O*-butyl-GlcA			

Fig. 1. Chemical structures of compounds **1** - **6**.

Table 2. Anti-complement activity of compounds **1** - **6** from the whole plant of *P. saniculaefolia*

Compound	IC_{50} (μM) [a]
oleanolic acid (**1**)	470.1
oleanonic acid (**2**)	212.2
23-hydroxyursolic acid (**3**)	121.0
3-*O*-α-L-arabinopyranosyl-oleanolic acid (**4**)	NE[c]
3-*O*-*β*-D-glucopyranosyl-oleanolic acid (**5**)	NE
oleanolic acid 3-*O*-[*β*-D-xylopyranosyl-(1 → 3)-*β*-D-glucuronopyranoside-6-*O*-butyl ester] (**6**)	NE
tiliroside[b]	86.1

[a]Results ane the mean (n = 3). [b]This compound was used as a positive control (Jung *et al*., 1998). [c] NE; no effect.

results obtained are summarized in Table 2 (IC_{50} values). Oleanolic acid (**1**), oleanonic acid (**2**), and 23-hydroxyursolic acid (**3**) showed anti-complement activity with IC_{50} values of 470.1, 212.2, and 121.0 μM, respectively, compared to tiliroside (IC_{50}, 86.1 μM), which was used as the positive control. On the other hand, 3-*O*-α-L-arabinopyranosyl-oleanolic acid (**4**), 3-*O*-*β*-D-glucopyranosyl-oleanolic acid (**5**), and oleanolic acid 3-*O*-[*β*-D-xylopyranosyl-(13)-*β*-D-glucuronopyranoside-6-*O*-butyl ester] (**6**) were completely incapable of inhibiting complement activity. Lee *et al*. also reported that oleanolic acid and oleanonic acid inhibited the complement system *in vitro* (Lee *et al*., 2004). On the other hand, ursane-type triterpenoids such as 23-hydroxyursolic acid (**3**) may have anti-complement activity active in this assay system. These data agreed with the anti-complement properties of ursolic acid, weigelic acid, esculentic acid, and asiatic acid isolated from *Weigela subsessilis*. (Thuong *et al*., 2006). These results demonstrate the role which the number of a carbonyl or hydroxy group at C-3 in the oleanane- and ursane-type triterpene was necessary for enhancing the anti-complement activity.

This is the first report on the isolation of compounds **1** - **6** from *P. saniculaefolia*.

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