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# Terpenoid constituents from *Youngia koidzumiana*

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**Abstract –** *Youngia koidzumiana* is an endemic plant growing in Mt. Chiri. In our ongoing research for endemic species in Korea, we investigated the chemical constituents from the MeOH extract of *Y. koidzumiana* whole plants. The MeOH extract was partitioned with hexane, ethyl acetate and BuOH, successively. Four known compounds were isolated from ethyl acetate fraction by repeated column chromatography. Their structures were elucidated by the physicochemical and spectral data as germanicol acetate (**1**), oleanolic acid (**2**), brachynereolide (**3**) and ixerin Y (**4**).

**Keywords –** *Youngia koidzumiana*, Compositae, germanicol acetate, oleanolic acid, brachynereolide, ixerin Y.

## Introduction

*Youngia koidzumiana* Kitamura (Compositae) is a wild plant growing in Mt. Chiri, Korea (Lee 1996). Although *Y. japonica* has been used as febrifuge and a remedy for snake bites (Perry 1980) and *Y. sonchifolia* as vegetable for Kimchi, *Y. koidzumiana* was not developed as any other food or medical usage. Several chemical components were reported from *Youngia* species such as guaiane-type sesquiterpenes like youngiaside A, B, C, D (Adegawa 1986 and Jang 2000), pentacyclic triterpenes as taraxasterol, beaurenyl acetate, α-, β-amyrin and γ-linolenic acid (Arai 1982 and Shin 1993). Recently, two cytotoxic compounds were isolated from *Y. japonica* and identified as 21α-hydroperoxy-taraxasterol and ursolic acid (Lee 2002). Up to now, the chemical components and biological activities of *Y. koidzumiana* has not been studied yet. In our ongoing research for Korean endemic plant, we investigated chemical constituents from the MeOH extract of *Y. koidzumiana* whole plants.

## Experimental

**Plant material –** The *Y. koidzumiana* whole plants were collected in the Mt. Chiri on November 2000 and identified by prof. KiHwan Bae, College of Pharmacy, Chungnam National University. The voucher specimens (CNU 20046) were deposited at the herbarium in the College of Pharmacy, Chungnam National University.

**Instruments –** The melting points were measured using a Yanagimoto micrio hot-stage melting point apparatus and was uncorrected. Both $^1$H- and $^{13}$C-NMR spectra were obtained from a Bruker DRX-300 NMR spectrometer. FAB-MS spectra were measured by Kratos Concept-1S Mass Spectrometer.

**Extraction and isolation –** The *Y. koidzumiana* whole plants (2 kg) were dried and extracted 3 times with MeOH to yield 120 g of a dried extract upon solvent removal under vacuum. The resulting extract was suspended in water and partitioned with hexane, ethyl acetate, and buthanol to afford 41.8 g, 48.8 g and 18.1 g residues, respectively. The ethyl acetate fraction was chromatgraphed on silica gel column with gradient hexane-ethyl acetate elution system (6:1 v/v to 100% ethyl acetate) to afford 7 fractions (Fr. A~H). Fr. A was taken into silica gel column chromatography with gradient hexane-chloroform solvent system (15:1-5:1) to give compound **1.** Compound **2** was isolated from Fr. D by silica gel column using hexane-chloroform-methanol solvent system (20:5:1). Fr. G was chromatographed on silica gel column to produce 5 subfractions (Subfr. A~E). The $C_{18}$ reverse phase column chromatography was used for Subfr. C and Subfr. D with methanol-water (2:1) as eluant to give compound **3** and **4**, respectively.

**Germanicol acetate (1)**: white powder (137 mg), mp 279-282°C. FAB-MS m/z: 491 $[M+Na]^+$. $^1$H-NMR (300 MHz, $CDCl_3$) δ : 4.88 (1H, s, H-19), 4.48 (1H, m, H-3α), 2.06 (3H, s, $\underline{CH_3}CO$), 1.10 (3H, s, H-27), 1.04 (3H, s, H-26), 0.97 (3H, s, H-25), 0.96 (3H, s, H-23), 0.93 (3H, s, H-29), 0.89 (3H, s, H-30), 0.87 (3H, s, H-24), 0.76 (3H, s, H-28). $^{13}$C-NMR (75 MHz, $CDCl_3$) δ : 39.0 (C-1), 24.1 (C-2), 81.3 (C-3), 38.2 (C-4), 56.0 (C-5), 18.5 (C-6), 34.9 (C-7), 41.2 (C-8), 51.5 (C-9), 37.5 (C-10), 21.5 (C-11), 26.5 (C-12),

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38.8 (C-13), 43.7 (C-14), 27.9 (C-15), 38.0 (C-16), 34.7 (C-17), 143.0 (C-18), 130.1 (C-19), 32.7 (C-20), 33.7 (C-21), 37.7 (C-22), 28.3 (C-23), 16.8 (C-24), 16.4 (C-25), 17.1 (C-26), 14.9 (C-27), 25.6 (C-28), 31.6 (C-29), 29.5 (C-30), 171.3 (<u>C</u>OO), 21.6 (<u>C</u>H$_3$COO).

**Oleanolic acid** (**2**): white powder (3.9 mg), mp 283-285°C. FAB-MS m/z: 479 $[M+Na]^+$. $^1$H-NMR (300 MHz, CDCl$_3$) δ : 5.30 (1H, m, H-12), 3.23 (1H, t, *J* = 4.1 Hz, H-3), 2.86 (3H, dd, *J* = 3.9, 13.5 Hz, H-18), 1.27 (3H, s, H-29), 1.15 (3H, s, H-30), 1.00 (3H, s, H-26), 0.93 (3H, br s, H-23), 0.93 (3H, br s, H-25), 0.79 (3H, s, H-27), 0.78 (3H, br s, H-24). $^{13}$C-NMR (75 MHz, CDCl$_3$) δ : 37.4 (C-1), 27.5 (C-2), 79.4 (C-3), 39.1 (C-4), 55.6 (C-5), 18.7 (C-6), 32.8 (C-7), 39.6 (C-8), 48.0 (C-9), 38.8 (C-10), 23.3 (C-11), 123.0 (C-12), 143.9 (C-13), 42.0 (C-14), 28.0 (C-15), 23.8 (C-16), 46.9 (C-17), 41.4 (C-18), 46.2 (C-19), 31.0 (C-20), 34.2 (C-21), 33.0 (C-22), 28.4 (C-23), 15.9 (C-24), 15.5 (C-25), 17.4 (C-26), 26.3 (C-27), 183.0 (C-28), 33.4 (C-29), 23.9 (C-30).

**Brachynereolide** (**3**): white needle (20 mg), mp 125-127°C. FAB-MS m/z: 433 $[M+Na]^+$. $^1$H-NMR (300 MHz, CD$_3$OD) δ : 6.06 (1H, d, *J* = 3.5 Hz, H-13α), 5.47 (1H, d, *J* = 3.5 Hz, H-13β), 5.10 (1H, br s, H-14α), 4.95 (1H, br s, H-14β), 4.59 (1H, d, *J* = 7.9 Hz, H-1) 3.18 (1H, t, *J* = 8.5 Hz, H-6), 1.32 (3H, s, H-14). $^{13}$C-NMR (75 MHz, CD$_3$OD) δ : Table 1.

**Ixerin Y** (**4**): white powder (6.5 mg), mp 180-182°C. FAB-MS m/z: 447 $[M+Na]^+$. $^1$H-NMR(300 MHz, CD$_3$OD) δ : 6.20 (1H, br s, H-13α), 6.11 (1H, br s, H-13β), 6.10 (1H, br s, H-3), 4.31 (1H, d, *J* = 7.8 Hz, H-1), 3.72 (1H, overlapped, H-8), 3.63 (1H, d, *J* = 6.5 Hz, H-5), 3.26 (1H, t, *J* = 8.0 Hz, H-6), 3.00 (1H, m, H-7), 1.78 (3H, s, H-14). $^{13}$C-NMR (75 MHz, CD$_3$OD) δ : Table 1.

**Table 1.** $^{13}$C-NMR Chemical Shifts of **3-4**

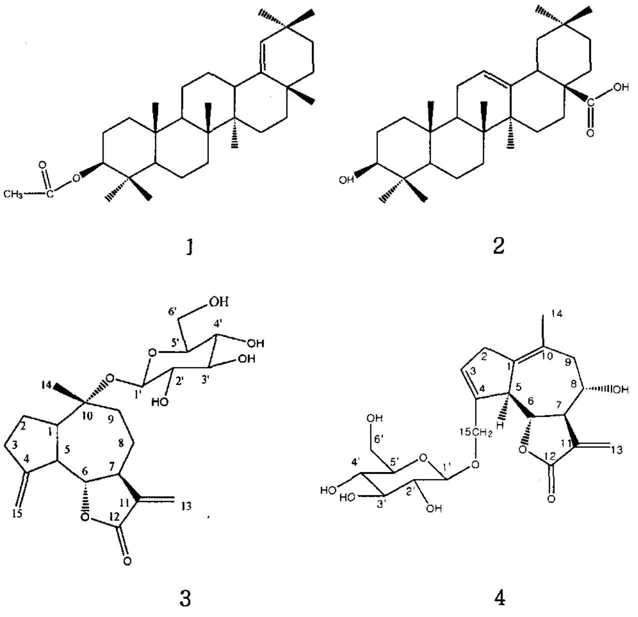
| No. of C | **3** | | **4** | |
|---|---|---|---|---|
| $C_1$ | 52.8 | CH | 137.0 | C |
| $C_2$ | 26.5 | $CH_2$ | 37.0 | $CH_2$ |
| $C_3$ | 29.4 | $CH_2$ | 130.0 | CH |
| $C_4$ | 151.3 | C | 141.0 | C |
| $C_5$ | 52.1 | CH | 52.3 | CH |
| $C_6$ | 81.3 | CH | 83.2 | CH |
| $C_7$ | 43.8 | CH | 58.2 | CH |
| $C_8$ | 24.0 | $CH_2$ | 68.7 | CH |
| $C_9$ | 30.9 | $CH_2$ | 45.6 | $CH_2$ |
| $C_{10}$ | 81.7 | C | 126.5 | C |
| $C_{11}$ | 143.1 | C | 139.0 | C |
| $C_{12}$ | 171.6 | C | 170.9 | C |
| $C_{13}$ | 118.1 | $CH_2$ | 120.9 | $CH_2$ |
| $C_{14}$ | 27.4 | $CH_3$ | 22.0 | $CH_3$ |
| $C_{15}$ | 109.0 | $CH_2$ | 67.8 | $CH_2$ |
| $C_1'$ | 97.5 | CH | 101.8 | CH |
| $C_2'$ | 74.3 | CH | 74.1 | CH |
| $C_3'$ | 77.5 | CH | 76.9 | CH |
| $C_4'$ | 70.6 | CH | 70.7 | CH |
| $C_5'$ | 76.4 | CH | 77.1 | CH |
| $C_6'$ | 61.7 | $CH_2$ | 61.8 | $CH_2$ |

## Results and discussion

The dried *Y. koidzumiana* whole plants were extracted with MeOH, which was further partitioned with hexane, ethyl acetate and buthanol, successively. By the repeated column chromatography of ethyl acetate fraction, four terpenoid compounds were afforded and identified by chemical and spectral data. The $^1$H-NMR spectrum of **1** showed 9 methyl singlet signals in which one at δ 2.06 (3H, s) was due to an acetate methyl signal. The singlet peak at δ 4.88 (1H, s) was identified as H-19 proton signal attached on an olefinic double bond. The methyl group in acetate residue was appeared at δ 21.6 and the chemical shift of C-3 carbon was appeared to downfield at δ 81.3 in the $^{13}$C-NMR spectrum. As the result, compound **1** was identified as germanicol acetate, which was reported from *Y. denticulata* (Gonzalez *et al.*, 1981).

The $^{13}$C-NMR spectrum of **2** was quite similar to that of **1** but it did not show the acetate methyl signal. The chemical shift of C-17 shifted downfield to δ 46.9 compared to that of **1** (δ 34.7) suggested that the carboxyl group was bonded to C-17 position. The $^1$H-NMR spectrum revealed a signal at δ 5.30 due to C-12 proton and the presence of a hydroxy group at C-3 with δ 3.23 (1H, t, *J* = 4.1 Hz). Thus compound **2** was identified as oleanolic acid (Shiojima *et al.*, 1995; Lee *et al.*, 2002).

For the compound **3**, the $^1$H-NMR spectrum showed two



1 2

3 4

**Fig. 1.** Structure of the compounds isolated from *Y. koidzumiana*.

signal at δ 6.06 (1H, d, $J$ = 3.5 Hz, H-13α) and δ 5.47 (1H, d, $J$ = 3.5 Hz, H-13β), which are characteristic of exocyclic methylene proton of the α-methylene-γ-lactone group common in sesquiterpene lactones. Two other signals at δ 5.10 (1H, br s) and δ 4.95 (1H, br s) were due to two protons attached at C-15. The $^{13}$C-NMR spectrum affirmed this observation by revealing two exocyclic methylenes at δ 118.1 and δ 109.0, respectively. The methyl signal of C-14 appeared at δ 27.4 and the sugar moiety C-1 at δ 97.5 suggested that the sugar moiety was attached to C-10. From the comparison of all spectra data of compound **3**, they were in good agreement with brachynereolide, which was reported from the genus *Brachylaena* (Zdero *et al.*, 1987).

In the case of **4**, the α-methylene-γ-lactone group was observed upon two signals at δ 6.20 (1H, br s, H-13α) and δ 6.11 (1H, br s, H-13β) in the $^1$H-NMR spectrum. The triplet signal at δ 3.26 (1H, $J$ = 8.0 Hz) attributed to the lactonic methine proton at C-6 indicated the *trans-diaxial* disposition between H-5 at δ 3.63 (1H, d, $J$ = 6.5 Hz) and H-7 at δ 3.00 (1H, m). Referring these chemical shifts with reported data (Ma *et al.*, 1999), this compound was assumed to have a β-hydroxy group at C-8 (δ 3.72, 1H, overlapped). In the $^{13}$C-NMR spectrum, 3 double bonds and a glucopyranosyl group signals were observed. A $CH_2$ signal of C-15 at δ 67.8 was shifted downfield in comparison with common hydroxymethylene groups affirming that the glucosidic position is at C-15 position. Based on the physicochemical and spectral data, the structure of **4** was determined as ixerin Y, which was isolated from *Ixeris denticulata* (Ma *et al.*, 1999).

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