# Two New Sesquiterpenes from the Aerial Parts of Pimpinella brachycarpa NAKAI 

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Pimpinella brachycarpa (Umbelliferae) is one of the most favored and increasingly popular wild vegetables grown in Asian regions. ${ }^{1,2}$ In particular, this plant has been used in Korean folk medicine for treating gastrointestinal disturbances, bronchial asthma, insomnia, and persistent cough. ${ }^{3}$ Terpenes, flavonoids, and essential oil components have been isolated from the herbs. ${ }^{3-5}$ Several biological activities of P. brachycarpa have been reported, including antibacterical, antioxidative, anti-proliferative, antifungal, and antithrombotic activities. ${ }^{6-9}$ We have recently reported the isolation of quinic acid derivatives with an anti-inflammatory effect from this plant. ${ }^{10}$ In continuing research on this source, two new sesquiterpenes ( $\mathbf{1}$ and $\mathbf{2}$ ) and ten known terpenes (3-12) were further isolated from the MeOH extracts. The structures were elucidated by means of spectroscopic methods and chemical evidence.
Compound 1 was obtained as a colorless gum, and its molecular formula $\mathrm{C}_{15} \mathrm{H}_{24} \mathrm{O}_{2}$ was inferred from the positive ion HR-FAB MS $m / z 237.1858[\mathrm{M}+\mathrm{H}]^{+}$(calcd. for 237.1855). The ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{1}$ (Table 1) displayed signals for two oxygenated methine proton signals at $\delta_{\mathrm{H}}=4.22(1 \mathrm{H}, \mathrm{m})$ and $4.33(1 \mathrm{H}, \mathrm{m})$, two exomethylenes at $\delta_{\mathrm{H}}=5.05,5.07$, 5.13 , and 5.24 (each $1 \mathrm{H}, \mathrm{s}$ ), one isopropenyl proton $\delta_{\mathrm{H}}=$
$1.73(3 \mathrm{H}, \mathrm{s})$ and $4.74(2 \mathrm{H}, \mathrm{s})$, a methine proton $\delta_{\mathrm{H}}=2.42$, and five methylene protons. Fifteen carbon signals appeared in the ${ }^{13} \mathrm{C}-\mathrm{NMR}$ spectrum, including one methyl carbon at $\delta_{\mathrm{C}}=19.9$, two oxygenated carbons at $\delta_{\mathrm{C}}=72.4$ and 74.3 , six olefinic carbons at $\delta_{\mathrm{C}}=110.2,111.4,113.5,150.5,150.7$, and 151.0 , five methylene carbons at $\delta_{\mathrm{C}}=25.6,29.8,32.4$, 33.2 , and 37.4 , and a methine carbon at $\delta_{\mathrm{C}}=39.9$. The ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY spectrum of 1 showed correlation signals at $\delta_{\mathrm{H}}=1.95$ and $2.27(\mathrm{H}-2) / 1.95$ and $2.40(\mathrm{H}-1)$ and $4.22(\mathrm{H}-3), 1.58$ and $1.64(\mathrm{H}-6) / 2.19$ and $2.22(\mathrm{H}-5)$ and $2.42(\mathrm{H}-7), 1.82$ and $1.93(\mathrm{H}-8) / 2.42(\mathrm{H}-7)$ and $4.33(\mathrm{H}-9)$, indicating the presence of partial structures (see bold lines in Figure 2). In the HMBC spectrum of $\mathbf{1}$, long-range correlations were observed between the following protons and carbons: $\mathrm{H}-1$ and $\mathrm{C}-3$, $\mathrm{C}-$ $9, \mathrm{C}-14 ; \mathrm{H}-3$ and $\mathrm{C}-5, \mathrm{C}-15$; $\mathrm{H}-7$ and $\mathrm{C}-9, \mathrm{C}-12, \mathrm{C}-13$; $\mathrm{H}-9$ and C-7, C-14; H-13 and C-7, C-12 (Figure 2). These spectral data led us to conclude that the planar structure of $\mathbf{1}$ is sinugibberodiol (3), which was isolated from Sinularia gibberosa. ${ }^{11}$ The optical rotation of $1\left([\alpha]_{\mathrm{D}}^{25}+8.6, \mathrm{CHCl}_{3}\right)$ was almost the same value but of the opposite sign to that of sinugibberodiol (3) $\left([\alpha]_{D}^{25}-5.0, \mathrm{CHCl}_{3}\right)$, suggesting that compound 1 could be a stereoisomer of sinugibberodiol (3). ${ }^{11,12}$ The relative configurations of the hydroxyl groups at

Table 1. ${ }^{1} \mathrm{H}-(500 \mathrm{MHz})$ and ${ }^{13} \mathrm{C}-\mathrm{NMR}(125 \mathrm{MHz})$ spectral data of $\mathbf{1 - 3}$ in $\mathrm{CDCl}_{3}$ ( $\delta$ in ppm)

| Position | 1 |  | 2 |  | 3 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\delta_{\mathrm{H}}$ | $\delta_{\text {C }}$ | $\delta_{\text {H }}$ | $\delta_{\mathrm{C}}$ | $\delta_{\mathrm{H}}$ | $\delta_{\text {C }}$ |
| 1 | $1.95 \mathrm{~m}, 2.40 \mathrm{~m}$ | 25.6 | $2.08 \mathrm{~m}, 2.28 \mathrm{~m}$ | 27.8 | $2.10 \mathrm{~m}, 2.30 \mathrm{~m}$ | 24.3 |
| 2 | $1.95 \mathrm{~m}, 2.27 \mathrm{~m}$ | 33.2 | $2.04 \mathrm{~m}, 2.09 \mathrm{~m}$ | 32.4 | 2.30 m | 32.7 |
| 3 | 4.22 m | 72.4 | 4.25 m | 75.5 | 4.22 m | 74.5 |
| 4 |  | 151.0 |  | 149.5 |  | 149.7 |
| 5 | $2.19 \mathrm{~m}, 2.22 \mathrm{~m}$ | 32.4 | $2.05 \mathrm{~m}, 2.40 \mathrm{~m}$ | 29.9 | $1.55 \mathrm{~m}, 2.40 \mathrm{~m}$ | 30.6 |
| 6 | $1.58 \mathrm{~m}, 1.64 \mathrm{~m}$ | 29.8 | $1.58 \mathrm{~m}, 1.65 \mathrm{~m}$ | 31.7 | $1.59 \mathrm{~m}, 1.64 \mathrm{~m}$ | 32.0 |
| 7 | 2.42 m | 39.9 | 2.52 m | 38.8 | 2.11 m | 41.1 |
| 8 | $1.82 \mathrm{~m}, 1.93 \mathrm{~m}$ | 37.4 | $1.89 \mathrm{~m}, 1.95 \mathrm{~m}$ | 36.6 | $1.64 \mathrm{~m}, 1.85 \mathrm{~m}$ | 37.0 |
| 9 | 4.33 m | 74.3 | 4.27 m | 73.6 | 4.00 m | 76.8 |
| 10 |  | 150.7 |  | 150.3 |  | 150.2 |
| 11 |  | 150.5 |  | 151.8 |  | 148.8 |
| 12 | 4.74 s | 110.2 | $4.73 \mathrm{~s}, 4.78 \mathrm{~s}$ | 110.1 | 4.76 s, 4.69 s | 110.2 |
| 13 | 1.73 s | 19.9 | 1.73 s | 19.4 | 1.69 s | 19.0 |
| 14 | $5.05 \mathrm{~s}, 5.13 \mathrm{~s}$ | 111.4 | $5.07 \mathrm{~s}, 5.19 \mathrm{~s}$ | 111.6 | 5.05 s, 5.10 s | 114.7 |
| 15 | $5.07 \mathrm{~s}, 5.24 \mathrm{~s}$ | 113.5 | 5.00 s, 5.18 s | 114.9 | 5.05 s, 5.19 s | 114.0 |

[^0] coupling constants in Hz in parentheses).


Figure 1. Chemical structures of 1-12.


1


2

Figure 2. Key ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY, HMBC , and NOESY correlations of 1 and 2.

C-3 and C-9 were established by the NOESY experiment (Figure 2), in which correlations between $\mathrm{H}-3\left(\delta_{\mathrm{H}}=4.22\right)$ and $\mathrm{H}-7\left(\delta_{\mathrm{H}}=2.42\right)$, and $\mathrm{H}-9\left(\delta_{\mathrm{H}}=4.33\right)$ and $\mathrm{H}-7\left(\delta_{\mathrm{H}}=\right.$ 2.42) were observed. The absolute configurations at C-3 and C-9 were determined by applying the modified Mosher's method (Figure 3). ${ }^{13}$ The results indicated that the absolute configurations of C-3 and C-9 were $S$ and $S$, respectively. Thus, the structure of $\mathbf{1}$ was established as $(3 S, 7 S, 9 S)-3,9-$ dihydroxygermacra-4(15),10(14),11(12)-triene.
Compound 2 was obtained as a colorless gum, and the molecular formula was determined to be $\mathrm{C}_{15} \mathrm{H}_{24} \mathrm{O}_{2}$ from the $[\mathrm{M}+\mathrm{H}]^{+}$peak at $m / z 237.1853$ (calcd. for 237.1855) in the HR-FAB MS spectrum. The NMR spectral data of 2 were very similar to those of compound $\mathbf{1}$, except for the chemical shift in C-3 $\left[\delta_{\mathrm{H}}=4.25(\mathrm{H}-3) ; \delta_{\mathrm{C}}=75.5(\mathrm{C}-3)\right.$ in $\mathbf{2} ; \delta_{\mathrm{H}}=4.22$ $(\mathrm{H}-3) ; \delta_{\mathrm{C}}=72.4(\mathrm{C}-3)$ in 1 ], which suggested that they have different stereochemistry of the hydroxyl group at C-3. The NOESY correlations were observed between $\mathrm{H}-7\left(\delta_{\mathrm{H}}=2.52\right)$ and H-9 $\left(\delta_{\mathrm{H}}=4.27\right)$, but no correlations were found between $\mathrm{H}-3\left(\delta_{\mathrm{H}}=4.25\right)$ and $\mathrm{H}-7\left(\delta_{\mathrm{H}}=2.52\right)$ (Figure 2). The absolute configurations at C-3 and C-9 were determined using the modified Mosher's method to be $3 R$ and $9 S$ (Figure 3). Therefore, the structure of $\mathbf{2}$ was established as $(3 R, 7 S, 9 S)$ -3,9-dihydroxygermacra-4(15),10(14),11(12)-triene.

Although compound $\mathbf{3}$ (sinugibberodiol) has been reported previously, ${ }^{11}$ the absolute configuration of the compound



1b: R = (R)-MTPA
1c: $\mathrm{R}=(\mathrm{S})$-MTPA


2c: $\mathrm{R}=(\mathrm{S})$-MTPA

$3 \mathrm{~b}: \mathrm{R}=(R)$-MTPA
$3 \mathbf{c}: \mathrm{R}=(S)$-MTPA

Figure 3. Values of $\delta_{\mathrm{S}}-\delta_{\mathrm{R}}$ (data obtained in pyridine- $d_{5}$ ) for the MTPA esters of 1-3.
was not determined. The absolute configurations at C-3 and $\mathrm{C}-9$ in 3 were determined to be $3 R$ and $9 R$ using the modified Mosher's method (Figure 3). Thus, the structure of 3 was established as ( $3 R, 7 R, 9 R$ )-3,9-dihydroxygermacra-4(15),10(14),11(12)-triene.

The structures of the other known compounds (4-11) were identified as $6 \beta, 14$-epoxyeudesm- $4(15)$-en-1 $\beta$-ol (4), ${ }^{14} 6 a$ -methoxyeudesm-4(15)-en-1 $\beta$-ol (5), ${ }^{14}$ (7R*)-opposit-4(15)-ene-1 $\beta, 7$-diol (6), ${ }^{14} 7 \beta$-methoxy-4(14)-oppositen-1 $\beta$-ol (7), ${ }^{15}$ ( $2 R^{*}, 6 S^{*}$ )-2,6-dihydroxyhumlaobtusa (8), ${ }^{16} 3 \alpha$-hydroxy-5,6-epoxy-7-megastigmen-9-one (9), ${ }^{16}(1 R, 6 R, 9 R)-6,9,11$ -trihydroxy-4-megastigmen-3-one (10), ${ }^{17}$ grasshopper ketone (11), ${ }^{18}$ and loliolide (12) ${ }^{18}$ by comparing their spectroscopic data with data in the literature.

## Experimental Section

Plant Material. The aerial parts of P. brachycarpa were collected at Taebaek mountain in Gangwon-Do province, Korea in May 2009 and the plant was identified by one of the authors (K.R. Lee). A voucher specimen (SKKU-09-09) was deposited in the herbarium of the School of Pharmacy, Sungkyunkwan University, Suwon, Korea.

Extraction and Isolation. The aerial parts of P. brachycarpa ( 5 kg ) were extracted with $80 \% \mathrm{MeOH}$ three times at room temperature. The resulting MeOH extracts ( 480 g ) were suspended in distilled water ( $800 \mathrm{~mL} \times 3$ ) and then successively partitioned with $n$-hexane, $\mathrm{CHCl}_{3}, \mathrm{EtOAc}$, and $n$ - BuOH , yielding residues weighing $43 \mathrm{~g}, 5 \mathrm{~g}, 13 \mathrm{~g}$, and 33 g , respectively. The purification of twelve compounds (1-12) is described in Supplementary Material.
(3S,7S,9S)-3,9-Dihydroxygermacra-4(15),10(14),11(12)-
triene (1). Colorless gum; $[\alpha]_{\mathrm{D}}^{25}+8.6\left(c 0.15, \mathrm{CHCl}_{3}\right)$; IR (KBr) $v_{\text {max }} 3380,2946,2833,1663,1452,1115,1032,677$ $\mathrm{cm}^{-1} ;{ }^{1} \mathrm{H}-\mathrm{NMR}$ and ${ }^{13} \mathrm{C}-\mathrm{NMR}$ data, see Table 1; FAB-MS $m / z 273[\mathrm{M}+\mathrm{H}]^{+}$; HR-FAB-MS $m / z 273.1858[\mathrm{M}+\mathrm{H}]^{+}$; (calcd. for $\mathrm{C}_{15} \mathrm{H}_{25} \mathrm{O}_{2}, 273.1855$ ).
(3R,7S,9S)-3,9-Dihydroxygermacra-4(15),10(14),11(12)triene (2). Colorless gum; $[\alpha]_{\mathrm{D}}^{25}-8.0\left(c 0.13, \mathrm{CHCl}_{3}\right)$; IR (KBr) $v_{\text {max }} 3383,2947,2833,1653,1453,1115,1032,694$ $\mathrm{cm}^{-1} ;{ }^{1} \mathrm{H}-\mathrm{NMR}$ and ${ }^{13} \mathrm{C}-\mathrm{NMR}$ data, see Table 1; FAB-MS $m / z 273[\mathrm{M}+\mathrm{H}]^{+}$; HR-FAB-MS $m / z 273.1853[\mathrm{M}+\mathrm{H}]^{+}$; (calcd. for $\mathrm{C}_{15} \mathrm{H}_{25} \mathrm{O}_{2}, 273.1855$ ).

Preparation of the ( $R$ )-MTPA Ester and ( $\boldsymbol{S}$ )-MTPA Ester from Compounds $\mathbf{1 - 3} .{ }^{13}$ Compound $\mathbf{1}(0.5 \mathrm{mg})$, in deuterated pyridine ( 0.2 mL ), was transferred to a clean NMR tube. (S)-(+)- $\alpha$-(Trifluoromethyl)phenylacetyl chloride ( $5 \mu \mathrm{~L}$ ) was immediately added under a $\mathrm{N}_{2}$ gas stream, and the NMR tube was permitted to stand at room temperature overnight. When the reaction was completed, it afforded the $(R)$-MTPA ester derivative (1b) of $\mathbf{1}$. In the same manner as described for $\mathbf{1 b}$, the $(S)$-MTPA ester derivative ( $\mathbf{1} \mathbf{c})$ of $\mathbf{1}$ was obtained. Similarly, treatment of 2 and 3 with $(S)$ - and $(R)$-MTPA afforded the respective Mosher esters $\mathbf{2 b}, \mathbf{2 c}, \mathbf{3 b}$, and $\mathbf{3 c}$. The ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of $\mathbf{1 b}, \mathbf{1 c}, \mathbf{2 b}, \mathbf{2 c}, \mathbf{3 b}$, and $\mathbf{3 c}$ were measured in NMR reaction tubes.
Compound 1b: Colorless gum; ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (Pyridine- $d_{5}$, $500 \mathrm{MHz}) \delta 1.760(2 \mathrm{H}, \mathrm{m}, \mathrm{H}-8), 2.350(2 \mathrm{H}, \mathrm{m}, \mathrm{H}-2), 5.024$ $\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{a}}-14\right), 5.056\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{a}}-15\right), 5.181\left(2 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{b}}-14\right.$, 15), $5.630(1 \mathrm{H}, \mathrm{m}, \mathrm{H}-3), 5.812(1 \mathrm{H}, \mathrm{m}, \mathrm{H}-9)$.

Compound 1c: Colorless gum; ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (Pyridine- $d_{5}$, $500 \mathrm{MHz}) \delta 1.695(2 \mathrm{H}, \mathrm{m}, \mathrm{H}-8), 2.328(2 \mathrm{H}, \mathrm{m}, \mathrm{H}-2), 5.126$ $\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{a}}-14\right), 5.222\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{a}}-15\right), 5.235\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{b}}-14\right)$, $5.267\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{b}}-15\right), 5.714(1 \mathrm{H}, \mathrm{m}, \mathrm{H}-3), 5.808(1 \mathrm{H}, \mathrm{m}, \mathrm{H}-$ $9)$.

Compound 2b: Colorless gum; ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (Pyridine- $d_{5}$, $500 \mathrm{MHz}) \delta 1.888\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{a}}-8\right), 1.944\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{b}}-8\right), 2.049$ $\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{a}}-2\right), 2.141\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{b}}-2\right), 5.030\left(2 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{a}}-14,15\right)$, $5.049\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{b}}-14\right), 5.268\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{b}}-15\right), 5.723(1 \mathrm{H}, \mathrm{m}, \mathrm{H}-$ 9), 5.688 ( $1 \mathrm{H}, \mathrm{m}, \mathrm{H}-3$ ).

Compound 2c: Colorless gum; ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (Pyridine- $d_{5}$, $500 \mathrm{MHz}) \delta 1.800\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{a}}-8\right), 1.893\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{b}}-8\right), 2.121$ $\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{a}}-2\right), 2.201\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{b}}-2\right), 4.986\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{a}}-15\right)$, $5.166\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{a}}-14\right), 5.230\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{b}}-15\right), 5.247\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{b}}-\right.$ 14), $5.749(1 \mathrm{H}, \mathrm{m}, \mathrm{H}-9), 5.715(1 \mathrm{H}, \mathrm{m}, \mathrm{H}-3)$.

Compound 3b: Colorless gum; ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (Pyridine- $d_{5}$, $500 \mathrm{MHz}) \delta 1.525\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{a}}-8\right), 1.776\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{b}}-8\right), 2.100$ $(2 \mathrm{H}, \mathrm{m}, \mathrm{H}-2), 5.097\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{a}}-14\right), 5.273\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{a}}-15\right)$, $5.284\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{b}}-14\right), 5.346\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{b}}-15\right), 5.560(1 \mathrm{H}, \mathrm{m}, \mathrm{H}-$ 9), 5.788 ( $1 \mathrm{H}, \mathrm{m}, \mathrm{H}-3$ ).

Compound 3c: Colorless gum; ${ }^{1} \mathrm{H}-\mathrm{NMR}$ (Pyridine- $d_{5}$,
$500 \mathrm{MHz}) \delta 1.561\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{a}}-8\right), 1.843\left(1 \mathrm{H}, \mathrm{m}, \mathrm{H}_{\mathrm{b}}-8\right), 2.134$
( $2 \mathrm{H}, \mathrm{m}, \mathrm{H}-2$ ), $5.046\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{a}}-14\right), 5.219\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{a}}-15\right)$, $5.232\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{b}}-14\right), 5.275\left(1 \mathrm{H}, \mathrm{s}, \mathrm{H}_{\mathrm{b}}-15\right), 5.543(1 \mathrm{H}, \mathrm{m}, \mathrm{H}-$ 9), $5.754(1 \mathrm{H}, \mathrm{m}, \mathrm{H}-3)$.

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Supporting Information. Spectral data of compounds 1 and 2, general experimental procedures, and the isolation details are available upon request from the corresponding author.

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[^0]:    Assignments were based on 2D NMR including COSY, HMQC and HMBC (Well-resolved couplings are expressed with coupling patterns and

