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.\(^4\,^5\) Several biological activities of \(P.\) brachycarpa have been reported, including antibacterial, 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 (1 and 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 \(C_{15}H_{26}O_8\) was inferred from the positive ion HR-FAB MS \(m/z\) 237.1858 \([M + H]^+\) (calcd. for 237.1855). The \(^1\)H-NMR spectrum of 1 (Table 1) displayed signals for two oxygenated methine proton signals at \(\delta_H = 4.22 (1H, m)\) and \(4.33 (1H, m)\), two exomethylenes at \(\delta_H = 5.05, 5.07, 5.13,\) and 5.24 (each \(1H, s\)), one isopropenyl proton \(\delta_H = 1.73 (3H, s)\) and 4.74 (2H, s), a methine proton \(\delta_H = 2.42,\) and five methylene protons. Fifteen carbon signals appeared in the \(^13\)C-NMR spectrum, including one methyl carbon at \(\delta_C = 19.9,\) two oxygenated carbons at \(\delta_C = 72.4\) and 74.3, six olefinic carbons at \(\delta_C = 110.2, 111.4, 113.5, 150.5, 150.7,\) and 151.0, five methylene carbons at \(\delta_C = 25.6, 29.8, 32.4, 33.2,\) and 37.4, and a methine carbon at \(\delta_C = 39.9.\) The \(^1\)H-\(^1\)H COSY spectrum of 1 showed correlation signals at \(\delta_H = 1.95\) and 2.27 (H-2)/1.95 and 2.40 (H-1) and 4.22 (H-3), 1.58 and 1.64 (H-6/2.19 and 2.22 (H-5) and 4.22 (H-7), 1.82 and 1.93 (H-8)/2.42 (H-7) and 4.33 (H-9), indicating the presence of partial structures (see bold lines in Figure 2). In the HMBC spectrum of 1, long-range correlations were observed between the following protons and carbons: H-1 and C-3, 3, 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 1 is sinugibberodiol (3), which was isolated from Sinularia gibberosa.\(^1\) The optical rotation of 1 \((\alpha)_D^{25} +8.6, \text{CHCl}_3\) was almost the same value but of the opposite sign to that of sinugibberodiol (3) \((\alpha)_D^{25} −5.0, \text{CHCl}_3\), suggesting that compound 1 could be a stereoisomer of sinugibberodiol (3).\(^1\)\(^1\)\(^2\) The relative configurations of the hydroxyl groups at

**Table 1.** \(^1\)H- (500 MHz) and \(^13\)C-NMR (125 MHz) spectral data of 1-3 in CDCl\(_3\) (δ in ppm)

<table>
<thead>
<tr>
<th>Position</th>
<th>(\delta_H)</th>
<th>(\delta_C)</th>
<th>(\delta_H)</th>
<th>(\delta_C)</th>
<th>(\delta_H)</th>
<th>(\delta_C)</th>
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<tr>
<td>1</td>
<td>1.95 m, 2.40 m</td>
<td>25.6</td>
<td>2.08 m, 2.28 m</td>
<td>27.8</td>
<td>2.10 m, 2.30 m</td>
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<td>2</td>
<td>1.95 m, 2.27 m</td>
<td>33.2</td>
<td>2.04 m, 2.09 m</td>
<td>32.4</td>
<td>2.30 m</td>
<td>32.7</td>
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<tr>
<td>3</td>
<td>4.22 m</td>
<td>72.4</td>
<td>4.25 m</td>
<td>75.5</td>
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<td>74.5</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>151.0</td>
<td></td>
<td>149.5</td>
<td></td>
<td>149.7</td>
</tr>
<tr>
<td>5</td>
<td>2.19 m, 2.22 m</td>
<td>32.4</td>
<td>2.05 m, 2.40 m</td>
<td>29.9</td>
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<tr>
<td>6</td>
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<td>29.8</td>
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<td>7</td>
<td>2.42 m</td>
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<td>2.52 m</td>
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</table>

Assignments were based on 2D NMR including COSY, HMQC and HMBC (Well-resolved couplings are expressed with coupling patterns and coupling constants in Hz in parentheses).

Key Words: Pimpinella brachycarpa, Umbelliferae, Sesquiterpene
C-3 and C-9 were established by the NOESY experiment (Figure 2), in which correlations between H-3 (δH = 4.22) and H-7 (δH = 2.42), and H-9 (δH = 4.33) and H-7 (δH = 2.42) were observed. The absolute configurations at C-3 and C-9 were determined by applying the modified Mosher’s method (Figure 3).

The results indicated that the absolute configurations of C-3 and C-9 were S and S, respectively. Thus, the structure of 1 was established as (3S,7S,9S)-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 C15H24O2 from the [M + 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 1, except for the chemical shift in C-3 [δH = 4.25 (H-3); δC = 75.5 (C-3) in 2; δH = 4.22 (H-3); δC = 72.4 (C-3) in 1], which suggested that they have different stereochemistry of the hydroxyl group at C-3. The NOESY correlations were observed between H-7 (δH = 2.52) and H-9 (δH = 4.27), but no correlations were found between H-3 (δH = 4.25) and H-7 (δH = 2.52) (Figure 2). The absolute configurations at C-3 and C-9 were determined using the modified Mosher’s method to be 3R and 9S (Figure 3).

Therefore, the structure of 2 was established as (3R,7S,9S)-3,9-dihydroxygermacra-4(15),10(14),11(12)-triene.

Although compound 3 (sinugibberodiol) has been reported previously,11 the absolute configuration of the compound was not determined. The absolute configurations at C-3 and C-9 in 3 were determined to be 3R and 9R using the modified Mosher’s method (Figure 3). Thus, the structure of 3 was established as (3R,7R,9R)-3,9-dihydroxygermacra-4(15),10(14),11(12)-triene.

The structures of the other known compounds (4-11) were identified as 6β,14-epoxyeudesm-4(15)-en-1β-ol (4),14 6α-methoxyeudesm-4(15)-en-1β-ol (5),14 (7R*)-opposit-4(15)-ene-1β,7-diol (6),14 7β-methoxy-4(14)-oppositen-1β-ol (7),15 (2R*,6S*)-2,6-dihydroxynuclastus (8),16 3α-hydroxy-5,6-epoxy-7-megastigmen-9-one (9),16 (1R,6R,9R)-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% MeOH three times at room temperature. The resulting MeOH extracts (480 g) were suspended in distilled water (800 mL × 3) and then successively partitioned with n-hexane, CHCl3, EtOAc, and n-BuOH, yielding residues weighing 43 g, 5 g, 13 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; [α]D25 +8.6 (c 0.15, CHCl3); IR (KBr) vmax 3380, 2946, 2833, 1663, 1452, 1115, 1032, 677 cm⁻¹; 1H-NMR and 13C-NMR data, see Table 1; FAB-MS m/z 273 [M + H]⁺; HR-FAB-MS m/z 273.1858 [M + H]⁺; (cald. for C₁₂H₂₀O₂, 273.1855).

(3R,7S,9S)-3,9-Dihydroxygermacra-4(15),10(14),11(12)-trienes (2). Colorless gum; [α]D25 −8.0 (c 0.13, CHCl3); IR (KBr) vmax 3383, 2947, 2833, 1653, 1453, 1115, 1032, 694 cm⁻¹; 1H-NMR and 13C-NMR data, see Table 1; FAB-MS m/z 273 [M + H]⁺; HR-FAB-MS m/z 273.1853 [M + H]⁺; (cald. for C₁₂H₂₀O₂, 273.1855).

Preparation of the (R)-MTPA Ester and (S)-MTPA Ester from Compounds 1-3. Compound 1 (0.5 mg), in deuterated pyridine (0.2 mL), was transferred to a clean NMR tube. (S)-(+)-α-Trifluoromethyl)phenylacetyl chloride (5 μL) was immediately added under a N₂ 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 1. In the same manner as described for 1b, the (S)-MTPA ester derivative (1c) of 1 was obtained. Similarly, treatment of 2 and 3 with (S)- and (R)-MTPA afforded the respective Mosher esters 2b, 2c, 3b, and 3c. The 1H-NMR spectra of 1b, 1c, 2b, 2c, 3b, and 3c were measured in NMR reaction tubes.

**Compound 1b:** Colorless gum; 1H-NMR (Pyridine-d₅, 500 MHz) δ 1.760 (2H, m, H-8), 2.350 (2H, m, H-2), 5.024 (1H, s, H₁₄-15), 5.056 (1H, s, H₁₄-15), 5.181 (2H, s, H₁₄-15), 5.362 (1H, m, H-3), 5.812 (1H, m, H-9).

**Compound 1c:** Colorless gum; 1H-NMR (Pyridine-d₅, 500 MHz) δ 1.695 (2H, m, H-8), 2.328 (2H, m, H-2), 5.126 (1H, s, H₁₄-15), 5.222 (1H, s, H₁₄-15), 5.235 (1H, s, H₁₄-15), 5.267 (1H, s, H₁₄-15), 5.714 (1H, m, H-3), 5.808 (1H, m, H-9).

**Compound 2b:** Colorless gum; 1H-NMR (Pyridine-d₅, 500 MHz) δ 1.888 (1H, m, H₁₄-15), 1.944 (1H, m, H₁₄-15), 2.049 (1H, m, H₁₄-15), 2.141 (1H, m, H₁₄-15), 5.030 (2H, s, H₁₄-15), 5.049 (1H, s, H₁₄-15), 5.268 (1H, s, H₁₄-15), 5.723 (1H, m, H-9), 5.688 (1H, m, H-3).

**Compound 2c:** Colorless gum; 1H-NMR (Pyridine-d₅, 500 MHz) δ 1.800 (1H, m, H₁₄-15), 1.893 (1H, m, H₁₄-15), 2.121 (1H, m, H₁₄-15), 2.201 (1H, m, H₁₄-15), 4.986 (1H, s, H₁₄-15), 5.166 (1H, s, H₁₄-15), 5.230 (1H, s, H₁₄-15), 5.247 (1H, s, H₁₄-15), 5.749 (1H, m, H-9), 5.715 (1H, m, H-3).

**Compound 3b:** Colorless gum; 1H-NMR (Pyridine-d₅, 500 MHz) δ 1.525 (1H, m, H₁₄-15), 1.776 (1H, m, H₁₄-15), 2.100 (2H, m, H-2), 5.097 (1H, s, H₁₄-15), 5.273 (1H, s, H₁₄-15), 5.284 (1H, s, H₁₄-15), 5.346 (1H, s, H₁₄-15), 5.560 (1H, m, H-9), 5.788 (1H, m, H-3).

**Compound 3c:** Colorless gum; 1H-NMR (Pyridine-d₅, 500 MHz) δ 1.561 (1H, m, H₈-15), 1.843 (1H, m, H₈-15), 2.134 (2H, m, H-2), 5.046 (1H, s, H₈-14), 5.219 (1H, s, H₈-15), 5.232 (1H, s, H₈-14), 5.275 (1H, s, H₈-15), 5.543 (1H, m, H-9), 5.754 (1H, m, 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.

**References.**