FULL PAPER

Three New Chalcones from the Aerial Parts of *Angelica keiskei*

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Three new chalcones, 3′-carboxymethyl-4,2′-dihydroxy-4′-methoxychalcone (**1**), (±)-4,2′,4′-trihydroxy-3′-[(3-hydroxy-2,2-dimethyl-6-methylenecyclohexyl)methyl]chalcone (**2**), and 2′′-hydroxyangelichalcone (**3**), were isolated from the aerial parts of *Angelica keiskei* (Umbelliferae) together with five known compounds, artocarmitin A (**4**), (+)-*cis*-(3′*R*,4′*R*)-methylkhellactone (**5**), (−)-*trans*-(3′*R*,4′*S*)-methylkhellactone (**6**), 3,4-dihydroxanthotoxin (**7**), and (*Z*)-*p*-coumaryl alcohol (**8**). The known compounds **4** – **8** were identified from *A. keiskei* for the first time. The structures of **1** – **3** were elucidated by interpreting spectroscopic data including 1D- and 2D-NMR.

Keywords: Chalcones, Flavonoids, Phenolic compounds, *Angelica keiskei*, Umbelliferae.

Introduction

Angelica keiskei (Umbelliferae) is a hardy perennial herb [1], which is native to Japan and now widely cultivated in Korea. The aerial parts and roots of *A. keiskei* have been used to restore vitality and treat dysuria, dyschezia, and dysgalactia [2]. Chalcone compounds from *A. keiskei* were reported to have diverse biological activities, such as anticancer [2 – 4], anti-inflammatory [5], antiobesity [6] [7], antidiabetic [8], and antihypertensive [9] effects. In the present phytochemical study, three new chalcones, 3′-carboxymethyl-4,2′-dihydroxy-4′-methoxychalcone (**1**), (±)-4,2′,4′-trihydroxy-3′-[(3-hydroxy-2,2-dimethyl-6-methylenecyclohexyl)methyl]chalcone (**2**), and 2′′-hydroxyangelichalcone (**3**), were isolated from the aerial parts of *A. keiskei* together with five known compounds, artocarmitin A (**4**) [10], (+)-*cis*-(3′*R*,4′*R*)-methylkhellactone (**5**) [11], (−)-*trans*-(3′*R*,4′*S*)-methylkhellactone (**6**) [11], 3,4-dihydroxanthotoxin (**7**), and (*Z*)-*p*-coumaryl alcohol (**8**) [12] (*Fig. 1*).

Results and Discussion

Compound **1** was isolated as a yellow solid and exhibited a protonated molecular ion peak at *m*/*z* 329.1020 ([*M* + H]$^+$) in the HR-ESI-MS, consistent with the molecular formula $C_{18}H_{16}O_6$. The ^{1}H- and ^{13}C-NMR spectra of **1** (*Tables 1* and *2*) showed signals for a chalcone skeleton at δ(H) 7.63 (*d*, *J* = 8.8, H–C(2,6))/δ(C) 131.9 (C(2,6)), 6.85 (*d*, *J* = 8.8, H–C(3,5))/117.0 (C(3,5)), 7.67 (*d*, *J* = 15.2, H–C(α))/118.7 (C(α)), 7.80 (*d*, *J* = 15.2, H–C(β))/145.6 (C(β)), 6.64 (*d*, *J* = 9.2, H–C(5′))/103.4 (C(5′)), 8.03 (*d*, *J* = 9.2, H–C(6′))/131.4 (C(6′)), and δ(C) 194.2 (C=O) [13]. In the ^{1}H-NMR spectrum, a CH_2 group was observed as a broad *singlet* at low field, δ(H) 3.58 (CH_2(1′′)). An extra C=O C-atom signal resonated at δ(C) 179.9 (C(2′′)). The ^{1}H- and ^{13}C-NMR signals at δ(H) 3.90 (*s*, 3 H)/δ(C) 56.3 were assigned as an aromatic MeO group [14]. The CH_2 H-atoms at δ(H) 3.58 exhibited a HMBC correlation with C(2′′) (*Fig. 2*), indicating the presence of a -CH_2COOH group. The connectivity of the -CH_2COOH group to the chalcone skeleton at C(3′) was determined by the HMBCs CH_2(1′′)/C(2′), C(3′), and C(4′) (*Fig. 2*). The HMBC cross peak of MeO–C(4′)/C(4′) and NOE correlation between MeO–C(4′) and CH(5′) confirmed that the aromatic MeO group is apparent at C(4′). Thus, the structure of **1** was elucidated as a new compound, 3′-carboxymethyl-4,2′-dihydroxy-4′-methoxychalcone.

Compound **2** was obtained as a yellow solid and its molecular formula was determined as $C_{25}H_{28}O_5$ by the HR-ESI-MS analysis (*m*/*z* 409.2008, [*M* + H]$^+$). The ^{1}H- and ^{13}C-NMR spectra of **2** (*Tables 1* and *2*) exhibited characteristics of the 3′-substituted chalcone, as found for **1** [13]. In its ^{1}H- and ^{13}C-NMR spectra, an oxygenated CH group was observed at δ(H) 3.43 (*dd*, *J* = 8.2, 3.8, H–C(4′′))/δ(C) 77.7 (C(4′′)), three CH_2 groups at δ(H) 3.13 (*dd*, *J* = 13.4, 11.3, H_α–C(1′′)) and 2.80 (*dd*, *J* = 13.4, 3.7, H_β–C(1′′))/δ(C) 22.1 (C(1′′)), 2.52 (*ddd*, *J* = 12.8, 7.2, 5.4, H_{ax}–C(6′′)) and 1.93 (*m*, H_{eq}–C(6′′))/32.7 (C(6′′)), and 1.76 – 1.84 (*m*, H_a–C(5′′)) and 1.52 – 1.63 (*m*, H_b–C(5′′))/32.9 (C(5′′)), a CH group at δ(H) 2.57 (*dd*, *J* = 11.3, 3.7, H–C(2′′))/δ(C) 51.4 (C(2′′)), and two Me groups at δ(H)

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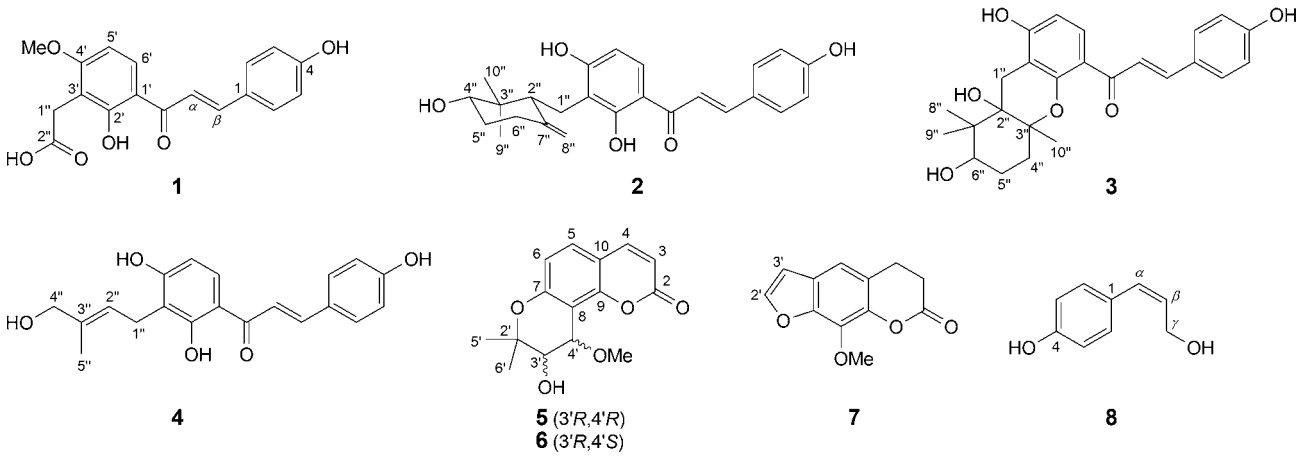

Fig. 1. Structures of compounds **1** – **3** from the aerial part of *A. keiskei*.

Table 1. ^{1}H-NMR data (400 MHz, CD_3OD) of compounds **1** – **3**[a]). Atom numbering as indicated in *Fig. 1*. δ in ppm, J in Hz.

H-atom	**1**	**2**	**3**
H–C(α)	7.67 (*d*, *J* = 15.2)	7.609 (*d*, *J* = 15.4)	7.618 (*d*, *J* = 15.2)
H–C(*β*)	7.80 (*d*, *J* = 15.2)	7.77 (*d*, *J* = 15.4)	7.80 (*d*, *J* = 15.2)
H–C(2,6)	7.63 (*d*, *J* = 8.8)	7.606 (*d*, *J* = 8.6)	7.620 (*d*, *J* = 8.8)
H–C(3,5)	6.85 (*d*, *J* = 8.8)	6.84 (*d*, *J* = 8.6)	6.84 (*d*, *J* = 8.8)
MeO–C(4′)	3.90 (*s*)		
H–C(5′)	6.64 (*d*, *J* = 9.2)	6.38 (*d*, *J* = 8.8)	6.38 (*d*, *J* = 8.8)
H–C(6′)	8.03 (*d*, *J* = 9.2)	7.79 (*d*, *J* = 8.8)	7.98 (*d*, *J* = 8.8)
CH_2(1″)	3.58 (br. *s*)	3.13 (*dd*, *J* = 13.4, 11.3, H_α)	3.30 (*d*, *J* = 16.6, H_a)
		2.80 (*dd*, *J* = 13.4, 3.7, H_β)	3.11 (*d*, *J* = 16.6, H_b)
H–C(2″)		2.57 (*dd*, *J* = 11.3, 3.7)	
CH_2(4″) or H–C(4″)		3.43 (*dd*, *J* = 8.2, 3.8)	1.93 – 1.96 (*m*, H_a)
			1.61 – 1.63 (*m*, H_b)
CH_2(5″)		1.76 – 1.84 (*m*, H_a)	1.94 – 1.98 (*m*, H_a)
		1.52 – 1.63 (*m*, H_b)	1.60 – 1.63 (*m*, H_b)
CH_2(6″) or H–C(6″)		2.52 (*ddd*, *J* = 12.8, 7.2, 5.4, H_{ax})	3.37 (br. *d*, *J* = 8.4)
		1.89 – 1.96 (*m*, H_{eq})	
CH_2(8″) or Me(8″)		4.68 (br. *s*, H_a), 4.59 (br. *s*, H_b)	0.90 (*s*)
Me(9″)		0.96 (*s*)	1.15 (*s*)
Me(10″)		1.06 (*s*)	0.98 (*s*)

[a]) Me_4Si was used as an internal standard.

1.06 (*s*, 3 H)/δ(C) 27.1 (C(10″)) and 0.96 (*s*, 3 H)/18.2 (C(9″)). And resonances at δ(H) 4.68 (br. *s*, H_a–C(8″)) and 4.59 (br. *s*, H_b–C(8″))/δ(C) 109.0 (C(8″)) were ascribed to the presence of an *exo*-CH_2 group. In the ^{13}C-NMR spectrum, two additional quaternary carbons appeared at δ(C) 41.6 (C(3″)) and 150.0 (C(7″)). The observation suggested the existence of a 3-hydroxy-2,2-dimethyl-6-methylenecyclohexylmethyl group [15][16]. The COSY correlations of H_α–C(1″)/H–C(2″), H_β–C(1″)/H–C(2″), H–C(4″)/H_b–C(5″), and H_a–C(5″)/H_{ax}–C(6″) and HMBC cross peaks of H_α–C(1″)/C(7″), H–C(2″)/C(3″), C(7″), Me(9″)/C(2″), C(3″), C(4″), Me(10″)/C(2″), C(3″), C(4″), H_{ax}–C(6″)/C(4″), C(7″), and H_a–C(8″)/C(2″), C(6″), and H_b–C(8″)/C(2″), C(6″) confirmed the assignments (*Fig. 2*). The 3-hydroxy-2,2-dimethyl-6-methylenecyclohexylmethyl group was assigned at C(3′) by the HMBC correlations of CH_2(1″)/C(2′), C(3′), and C(4′).

The relative configuration of **2** was determined by the NOESY correlations and coupling constants. The NOESY correlations of H_a–C(8″)/H_α–C(1″) and H–C(2″) and H_b–C(8″)/H_{ax}–C(6″) demonstrated that the *exo*-CH_2 group is parallel to the mean plane of the cyclohexane. The ^{1}H-^{1}H NOESY spectrum of **2** exhibited important correlations of H–C(2″)/H–C(4″) and H_{ax}–C(6″) (*Fig. 3*), which suggested that H–C(2″), H–C(4″), and H_{ax}–C(6″) are axial H-atoms on the same side of the cyclohexane. And, the NOESY cross peaks of Me(10″)/H–C(2″) and H–C(4″) indicated the same orientation of the Me group (C(10″)) with H–C(2″) and H–C(4″) on the cyclohexane. The axial orientation of H–C(4″) (in other words, the equatorial

Table 2. ^{13}C-NMR data (CD_3OD, 100 MHz) of compounds **1** – **3**[a]). Atom numbering as indicated in *Fig. 1*. δ in ppm.

C-atom	**1**	**2**	**3**
C(α)	118.7	118.7	118.4
C(β)	145.6	145.2	145.9
C=O	194.2	193.8	193.9
C(1)	128.0	128.0	127.7
C(2,6)	131.9	131.8	131.9
C(3,5)	117.0	117.0	117.1
C(4)	161.7	161.7	162.1
C(1′)	115.9	114.4	115.9
C(2′)	164.4	165.8	162.1
C(3′)	115.0	117.3	115.5
C(4′)	165.3	164.3	168.4
*Me*O–C(4′)	56.3		
C(5′)	103.4	108.4	102.4
C(6′)	131.4	130.3	133.6
C(1″)	31.9	22.1	29.8
C(2″)	179.9[b])	51.4	100.7
C(3″)		41.6	74.5
C(4″)		77.7	36.0
C(5″)		32.9	27.5
C(6″)		32.7	74.8
C(7″)		150.0	45.4
C(8″)		109.0	21.9
C(9″)		18.2	16.7
C(10″)		27.1	25.6

[a]) Me_4Si was used as an internal standard. [b]) Chemical shifts were estimated by HMBC NMR data.

orientation of OH group) was confirmed by the coupling constant values between H–C(4″) and CH_2 H-atoms of C(5″) ($^3J_{4''5''}$ = 8.2, 3.8 Hz). These actual ^3J values approximately corresponded to the expected $^3J_{HH}$ value ranges deduced from their dihedral angles, based on the *Karplus* relationship (Φ = 170°, $^3J_{HH}$ = 9 – 13 Hz; Φ = 53°, $^3J_{HH}$ = 2 – 6 Hz) [17]. However, when the molecular model was drawn with equatorial H–C(4″), the dihedral angles were calculated as 62° and 55° and the splitting pattern of H–C(4″) was expected as a broad *triplet* not the *doublet of doublet* as observed in its ^{1}H-NMR spectrum of **2** [15]. The CH_2 H-atoms at C(1″) showed diastereotopic characteristics and each was assigned as H_α–C(1″) and H_β–C(1″) by considering which actual coupling constant value ($^3J_{1''2''}$ = 11.3, 3.7 Hz) is adequate to the calculated dihedral angle ($\Phi_{1''2''}$ = 168, 53°), respectively [17]. For the overall computational calculations, the molecular modeling program (MM2 of SCIGRESS) was utilized to build the molecular models of **2**. The structure and relative configuration of the substituent in **2** were also confirmed by comparison with those in cordiaquinione L and M, naphthoquinone derivatives containing the same 3-hydroxy-2,2-dimethyl-6-methylenecyclohexyl group [15]. Compound **2** was determined as a racemic mixture with a specific rotation of $[\alpha]_D^{25} \pm 0$ (*c* 0.05, MeOH). From a biosynthetic point of view, it is assumed that the 3′-geranylated chalcones of *A. keiskei*

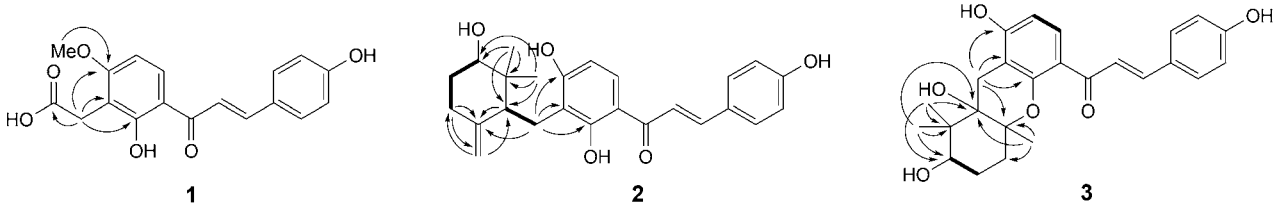

Fig. 2. Important ^{1}H,^{1}H-COSY (▬) and HMBC (H → C) data of **1** – **3**.

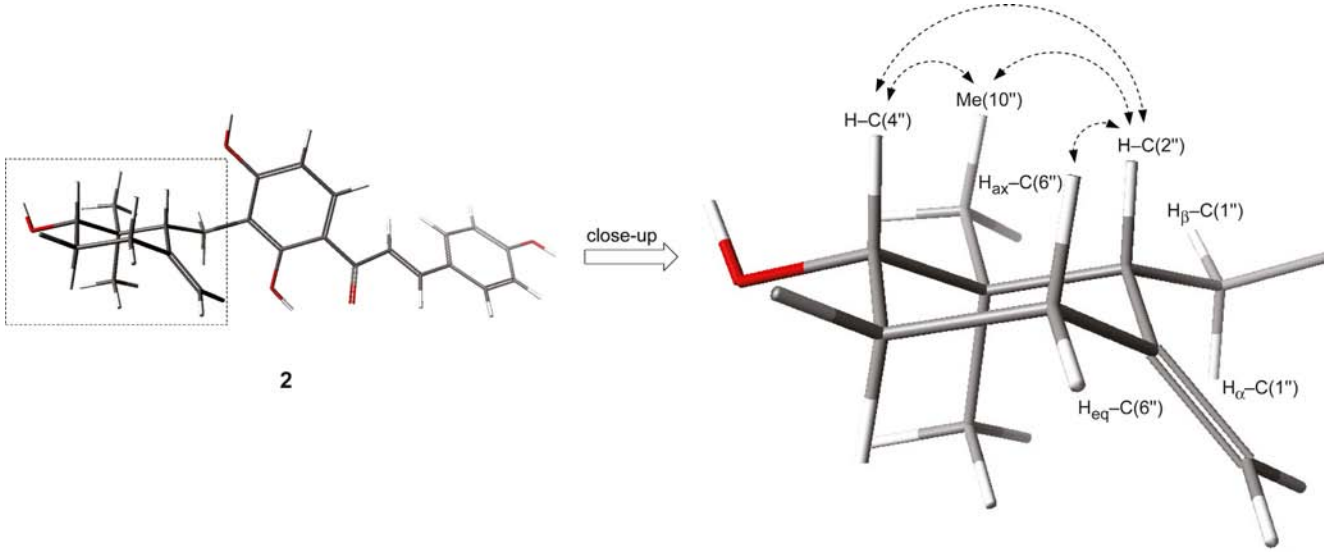

Fig. 3. Key ^{1}H,^{1}H-NOESY (H ↔ H) correlations in the energy-minimized structure of **2**.

serve as a precursor of **2** through ring formation at the geranyl group [18][19]. Moreover, the racemic nature of the chalcone compounds of *A. keiskei* [20 – 22] could be biosynthetically correlated with isolation of **2** as the racemic mixture. Therefore, the structure of **2** was elucidated as a new compound, (±)-4,2′,4′-trihydroxy-3′-[(3-hydroxy-2,2-dimethyl-6-methylenecyclohexyl)methyl]chalcone. The structure shown for **2** in *Fig. 1* is one of the two possible representations with the relative configuration.

Compound **3** was isolated as a yellow solid. Its molecular formula was established as $C_{25}H_{28}O_6$ by the HR-ESI-MS (*m*/*z* 425.1964 ([*M* + H]$^+$)). The ^{1}H- and ^{13}C-NMR spectra of **3** (*Tables 1* and *2*) also showed the typical signals for the 3′-substituted chalcone as those of **1** and **2** [13]. Three CH_2 group appeared at δ(H) 3.30 (*d*, *J* = 16.6, H_a–C(1″)) and 2.80 (*d*, *J* = 16.6, H_b–C(1″))/δ(C) 29.1 (C(1″)), 1.93 – 1.96 (*m*, H_a–C(4″)) and 1.61 – 1.63 (*m*, H_b–C(4″))/36.0 (C(4″)), and 1.94 – 1.98 (*m*, H_a–C(5″)) and 1.60 – 1.63 (*m*, H_b–C(5″))/27.5 (C(5″)), a CH group at δ(H) 3.37 (br. *d*, *J* = 8.4, H–C(6″))/δ(C) 74.8 (C(6″)), and three Me groups at δ(H) 0.90 (*s*, 3H)/δ(C) 21.9 (C(8″)), 1.15 (*s*, 3H)/16.7 (C(9″)), and 0.98 (*s*, 3H)/25.6 (C(10″)). These ^{1}H- and ^{13}C-NMR signals were comparable with those reported for angelichalcone, except for the absence of the H-atom signal corresponded to C(2″) [7] [23]. Instead, a quaternary C-atom signal was observed at δ(C) 100.7 (C(2″)), which indicated the presence of a OH group at C(2″) in **3**. The unambiguous assignments of all of the ^{1}H- and ^{13}C-NMR signals of **3** were allowed by further detailed analysis of ^{1}H,^{1}H-COSY, ^{1}H,^{1}H-NOESY, ^{1}H,^{13}C-HSQC, and ^{1}H,^{13}C-HMBC data (*Fig. 2*). Thus, the structure of **3** was elucidated as a new compound, 2″-hydroxyangelichalcone.

A result of a chiral HPLC-UV separation of **3** (column: ChiralPak IB, 250 × 4.6 mm; mobile phase: *n*-hexane/EtOH, 4:1, *v*/*v*; flow rate: 1 ml/min; detection: UV 365 nm) exhibited mainly two signals, indicating presence of a mixture of stereoisomers. Compound **3** is not a racemic mixture according to its specific rotation, $[\alpha]_D^{25} = -54$ (*c* = 0.1, MeOH). However, the stereoisomers in **3** could not be each purified and identified for lack of amount.

Compounds **4** – **8** were identified from this plant for the first time. Furthermore, **7** was reported only as the biological metabolite of xanthotoxin [24] and the synthetic intermediate of furocoumarin derivatives [25][26] without any available spectroscopic data. For determination of the absolute configurations at C(3′) and C(4′) of **5** and **6**, their CD data were compared to literature values reported for (+)-*cis*-(3′*R*,4′*R*)-khellactone and (−)-*trans*-(3′*R*,4′*S*)-khellactone, respectively [27].

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Experimental Part

General

Thin-layer chromatography (TLC): silica gel *60 F_{254}* (SiO_2) and *RP-18 F_{254s}* SiO_2 plates (*Merck*, Darmstadt, Germany); spot observation under UV light and visualization by spraying with 10% aq. H_2SO_4 soln., followed by heating at 120 °C for 5 min. Column chromatography (CC): SiO_2 (230 – 400 mesh; *Merck*), *YMC Gel ODS-A* (12 nm, *S-150* μm; *YMC*, Kyoto, Japan), and *Sephadex LH-20* (*GE Healthcare Bio-Sciences AB*, Uppsala, Sweden). Optical rotations: *JASCO P-1010* polarimeter. UV Spectra: *Hitachi U-3000* spectrophotometer; λ_{max} (log ε) in nm. Circular dichroism (CD) spectra: *Jasco J-810* CD-ORD spectropolarimeter (Tokyo, Japan); λ_{max} ($\Delta\varepsilon$) in nm. 1D- and 2D-NMR spectra: *Varian Unity INOVA* 400 MHz FT-NMR instrument (*Varian Inc.*, Palo Alto, CA, USA); δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. MS: *Waters ACQUITY UPLC* system coupled to a *Micromass Q-Tof Micro* mass spectrometer (*Waters Cooperation*, Milford, MA, USA) and *Agilent 6220 Accurate-Mass* TOF LC/MS system (*Agilent Technologies*, Santa Clara, CA, USA); in *m*/*z*.

Plant Material

The aerial parts of *A. keiskei* were purchased from the Chodamchae in Seoul, Korea and identified by Prof. *Je-Hyun Lee* (College of Oriental Medicine, Dongguk University). A voucher specimen (No. EA327) has been deposited at the Natural Product Chemistry Laboratory, College of Pharmacy, Ewha Womans University.

Extraction and Isolation

The aerial parts of *A. keiskei* (8 kg) were extracted with MeOH (2 × 12 l) overnight at room temperature. The solvent was evaporated *in vacuo*, affording a conc. MeOH extract (2.5 kg). This extract was suspended in MeOH/H_2O (19:1, 4 l) mixture and then fractionated with hexanes (5 × 4 l). The conc. MeOH/H_2O-soluble fraction was suspended in dist. H_2O and partitioned with AcOEt (5 × 4 l). The AcOEt extract (142 g) was chromatographed over CC (SiO_2; hexanes/AcOEt 99:1 → 1:1, AcOEt/MeOH 1:0 → 0:1): *Fractions 1 – 16*. *Fr. 11* (14 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH 199:1 → 4:1): *Frs. 11.01 – 11.16*. *Fr. 11.12* (9 g) was chromatographed over CC (*ODS-A*; MeOH/H_2O 2:3 → 4:1): *Frs. 11.12.01 – 11.12.22*. *Fr. 11.12.08* (625 mg) was purified by CC (*ODS-A*; MeOH/H_2O 1:1 → 3:2) to yield **5** (0.7 mg) and **6** (0.6 mg). *Fr. 11.15* (1 g) was separated by CC (*ODS-A*; MeOH/H_2O 1:1 → 7:3): *Frs. 11.15.01 – 11.15.15*. Fr. 11.15.01 (4 mg) was purified by *Sephadex LH-20* with 100% MeOH, affording **8** (0.5 mg). *Fr. 13* (3 g) was subjected to CC (SiO_2; $CHCl_3$/acetone 49:1 → 4:1): *Frs.*

13.01 – 13.21. *Fr. 13.20* (528 mg) was chromatographed over CC (*ODS-A*; MeOH/H_2O 9:11 → 4:1): *Frs. 13.20.01 – 13.20.22*. *Fr. 13.20.12* (69.9 mg) was purified by *Sephadex LH-20* with 100% MeOH to afford **3** (0.7 mg) and **4** (0.4 mg). *Fr. 15* (25 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH 99:1 → 9:1 $CHCl_3$/MeOH/H_2O 90:10:1 → 15:10:2): *Frs. 15.01 – 15.12. Fr. 15.06* (3 g) was chromatographed over CC (*ODS-A*; MeOH/water 1:1 → 9:1): *Frs. 15.06.01 – 15.06.17. Fr. 15.06.09* (11 mg) was separated by *Sephadex LH-20* with 100% MeOH to obtain **2** (0.5 mg). *Fr. 15.08* (820 mg) subjected to CC (*ODS-A*; MeOH/H_2O 2:3 → 9:1): *Frs. 15.08.01 – 15.08.24*. **7** (0.5 mg) was separated from *Fr. 15.08.06* (14 mg) by CC (*Sephadex LH-20*; 100% MeOH). *Fr. 15.12* (9 g) was chromatographed over CC (*ODS-A*; MeOH/water 2:3 → 4:1): *Frs. 15.12.01 – 15.12.21. Fr. 15.12.10* (60 mg) was purified by *Sephadex LH-20* with 100% MeOH affording **1** (0.7 mg).

{2-Hydroxy-3-[(2*E*)-3-(4-hydroxyphenyl)prop-2-enoyl]-6-methoxyphenyl}acetic Acid (**1**). Yellow amorphous solid. UV (MeOH): 365 (4.04). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. HR-ESI-MS: 329.1020 ([*M*+H]$^+$, $C_{18}H_{17}O_6^+$; calc. 329.1020).

(±)-(2*E*)-1-{2,4-Dihydroxy-3-[(3-hydroxy-2,2-dimethyl-6-methylidenecyclohexyl)methyl]phenyl}-3-(4-hydroxyphenyl) prop-2-en-1-one (**2**). Yellow amorphous solid. $[\alpha]_D^{25} = \pm 0$ (*c* = 0.05, MeOH). UV (MeOH): 368 (4.31). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. HR-ESI-MS: 409.2008 ([*M*+H]$^+$, $C_{25}H_{29}O_5^+$; calc. 409.2010).

2′′-Hydroxyangelichalcone (= **(2*E*)-1-(2,3,4,4a,9,9a-Hexahydro-2,8,9a-trihydroxy-1,1,4a-trimethyl-1*H*-xanthen-5-yl)-3-(4-hydroxyphenyl)-prop-2-en-1-one**; **3**). Yellow amorphous solid. $[\alpha]_D^{25} = -54$ (*c* = 0.1, MeOH). UV (MeOH): 369 (4.29). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. HR-ESI-MS: 425.1964 ([*M*+H]$^+$, $C_{25}H_{29}O_6^+$; calc. 425.1959).

3,4-Dihydroxanthotoxin (= **5,6-Dihydro-9-methoxy-7*H*-furo[3,2-*g*][1]benzopyran-7-one**; **7**). Colorless amorphous solid. UV (MeOH): 282 (3.08), 250 (3.36). ^{1}H-NMR (400 MHz, CD_3OD): 7.55 (*d*, *J* = 2.2, H–C(2′)); 7.02 (*s*, H–C(5)); 6.65 (*d*, *J* = 2.2, H–C(3′)); 4.05 (*s*, MeO–C(8)); 2.94 (*t*, *J* = 7.4, CH_2(4)); 2.53 (*t*, *J* = 7.4, CH_2(3)). ^{13}C-NMR (100 MHz, CD_3OD): 182.9 (C(2)); 147.0 (C(7)); 145.5 (C(9)); 144.9 (C(2′)); 134.2 (C(8)); 128.1 (C(10)); 122.7 (C(6)); 116.0 (C(5)); 107.6 (C(3′)); 61.0 (*Me*O–C(8)); 39.6 (C(3)); 28.4 (C(4)). HR-ESI-MS: 219.0650 ([*M*+H]$^+$, $C_{12}H_{11}O_4^+$; calc. 219.0652).

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