Development of Biologically Active Compounds from Edible Plant Sources XIV. Cyclohexylethanoids from the Flower of Campsis grandiflora K. Schum.

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\(\text{Campsis grandiflora} \) flower was extracted with 80% aqueous MeOH, and concentrated extract was successively partitioned with EtOAc, \(n\)-BuOH, and \(\text{H}_2\text{O}\). From \(n\)-BuOH fraction, two cyclohexylethanoids were isolated through repeated silica gel and Sephadex LH-20 column chromatographies. Based on physico-chemical data obtained from NMR, MS, and IR, chemical structures of compounds were determined as 1,4-dihydroxy-3,4-(epoxyethano)-5-cyclohexene (1) and cornoside (2). These compounds were isolated for the first time from \(C. \) grandiflora flower.

**Key words:** Campsis grandiflora, cyclohexylethanoid, 1,4-dihydroxy-3,4-(epoxy-ethano)-5-cyclohexene, cornoside.

\(\text{Campsis grandiflora} \) K. Schum. flower of this plant has been used as a traditional medicine in Korea and China, and as an ornamental plant in Japan. The chemical constituents of genus \(\text{Campsis} \) have been studied by a number of researchers, including iridoid and phenylpropanoid glycosides isolated from \(\text{Campsis chinensis} \). In addition, analyses of the essential oil, phenolics, and boron compounds \(\text{C. grandiflora} \) have been carried out. However, isolation of the chemical component from \(\text{C. grandiflora} \) has not yet been reported. Isolation of lipids from the flower of \(\text{C. grandiflora} \) and their inhibitory effect on FPTase,\(^*\) as well as the isolation of six cyclohexylethanoids including three new compounds from the flower of this plant have been reported (kim et al., in submission). Two cyclohexylethanoids were additionally isolated from this plant. This paper reports the isolation and structure determination of these compounds.

**Materials and Methods**

**Instruments.** Melting points were determined on an Fisher-John Apparatus and uncorrected. Optical rotations were measured on a JASCO P-1010 digital polarimeter. FAB-MS were recorded on a JEOL JMSAX 505-WA. IR spectra were run on a Perkin Elmer spectrum One FT-IR spectrometer. \(^1\)H-NMR (400 MHz) and \(^13\)C-NMR (100 MHz) spectra were taken on a Varian Unity Inova AS 400 FT-NMR spectrometer.

**Materials.** \(C. \) grandiflora K. Schum. flower was imported from China in March, 2003, and identified by Prof. Dae-Keun Kim, Woosuk University, Jeonju. A voucher specimen (KHU03061) was reserved at the Laboratory of Natural Products Chemistry, KyungHee University, Suwon, Korea.

**Isolation of cyclohexylethanoids.** The dried and powdered flower of \(\text{C. grandiflora} \) (6 kg) was extracted at r.t. with 80% aqueous MeOH (45 \(\times\) 3). The extracts were partitioned with water (4 \(l\)), EtOAc (4 \(l\) \(\times\) 3), and \(\text{H}_2\text{O}\) (4 \(l\) \(\times\) 3). The \(\text{H}_2\text{O}\) extract (CGB, 85 g) was applied to the silica gel column chromatography (c.c.) eluted with CHCl\(_3\) : MeOH (10 : 1), EtOAC : MeOH (4 : 3), and \(\text{H}_2\text{O}\) (4 : 3). The \(\text{H}_2\text{O}\) extract (CGB, 85 g) was applied to the silica gel column (Films, cm\(^2\)) with CHCl\(_3\) : MeOH (50 : 1) to produce 10 fractions (CGB3-1 to CGB3-10). CGB3-1 (179 mg) fraction was subjected to the silica gel c.c. (CHCl\(_3\)-benzene), m.p. 102.0° (Films, cm\(^2\)) eluted with CHCl\(_3\) : MeOH (10 : 1), and heated on the TLC to ultimately produce purified compound 1 (20 mg) showing the unique yellow color of a cyclohexylethanoid.

**Compound 1 [1,4-dihydroxy-3,4-(epoxyethano)-5-cyclohexenol]:** Colorless crystals (CHCl\(_3\)-benzene), m.p. 97-98°C; \(\alpha\)_\text{D} +102.0° \((c = 1.2, \text{MeOH})\); positive FAB/MS \(m/z\) 157(M+H)+; IR (Films, cm\(^{-1}\)) 3400, 1675; \(^1\)H-NMR(400 MHz, pyridine-d\(_5\)) \(\delta \) 6.15(1H, ddd, \(J = 9.8, 1.8, 1.0 \) Hz, H-6), 6.10(1H, dd, \(J = 9.8, 2.0 \) Hz, H-5), 4.58(1H, m, H-1), 4.49(1H, dd, \(J = 11.0, 4.8 \) Hz, H-3), 4.32(1H, ddd, \(J = 9.6, 8.0, 6.8 \) Hz, H-2\(\alpha\)),

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The flower of *Campsis grandiflora* K. Schum. was extracted with 80% aqueous MeOH, and the concentrated extract was successively partitioned with EtOAc, n-BuOH, and H₂O. From the n-BuOH fraction, two cyclohexylethanoids were isolated through repeated silica gel and Sephadex LH-20 column chromatographies.

**Fig. 1. Chemical structures of cyclohexylethanoids from the flower of *Campsis grandiflora* **K. Schum.**

The flower of *C. grandiflora* was extracted with 80% aqueous MeOH, and the concentrated extract was successively partitioned with EtOAc, n-BuOH, and H₂O. From the n-BuOH fraction, two cyclohexylethanoids were isolated through repeated silica gel and Sephadex LH-20 column chromatographies.

**Compound 1** (cornoside): Oils (CHCl₃-MeOH), [α]D -19.5° (c = 1.5, MeOH); positive FAB/MS m/z: 317(M+H)+; IR, (Films, cm⁻¹): 3410, 1710, 1690; ¹H-NMR(400 MHz, CD3OD, δ) 6.15(1H, d, J = 9.6 Hz, H-1'), 3.99(1H, dt, J = 10.0, 6.4 Hz, H-2'a), 3.63(1H, dt, J = 12.5, 4.8, 4.8, 1.0 Hz, H-2a), 2.25(1H, ddd, J = 9.6 Hz, H-3, 5), 6.11(each 1H, d, J = 12.5, 11.0, 9.6 Hz, H-2b); 13C-NMR(100 MHz, pyridine-δ₆) 133.2(C-6), 130.6(C-5), 83.4(C-3), 76.9(C-4), 67.2(C-2), 65.3(C-1), 39.8(C-1'), 39.7(C-2).

**Compound 2** (cornoside): Oils (CHCl₃-MeOH), [α]D -19.5° (c = 1.5, MeOH); positive FAB/MS m/z: 317(M+H)+; IR, (Films, cm⁻¹): 3410, 1710, 1690; ¹H-NMR(400 MHz, CD3OD, δ) 6.15(1H, d, J = 9.6 Hz, H-1'), 3.99(1H, dt, J = 10.0, 6.4 Hz, H-2'a), 3.63(1H, dt, J = 7.6 Hz, H-1''), 3.92 (1H, d), and several oxygenated methine and methylene signals at δ3.53. In addition, an oxygenated ethyl group. In the ¹C-NMR spectrum, 14 signals including two olefinic methine, oxygenated methylene, and methylene at δ3.53. To confirm the position of each carbon, 2D-NMRs including gCOSY, gHSQC, and gHMBC were performed. A series of the partial structure was inferred by gCOSY, and the carbon and proton signals were exactly assigned by gHSQC. In addition, based on the spectrum of gHMBC, sites of the functional groups were verified. Through comparison of these NMR data with those in the literature, compound 1 was identified as 1,4-dihydroxy-3,4-(epoxyethano)-5-cyclohexene, previously isolated from *Millingtonia hortensis*.

**Results and Discussion**

The flower of *C. grandiflora* was extracted with 80% aqueous MeOH, and the concentrated extract was successively partitioned with EtOAc, n-BuOH, and H₂O. From the n-BuOH fraction, two cyclohexylethanoids were isolated through repeated silica gel and Sephadex LH-20 column chromatographies.

**Compound 1**, colorless crystals, showed absorbance bands at 3400 and 1675cm⁻¹ in the IR spectrum (MeOH) due to hydroxyl and double bond, respectively, and a molecular ion peak (M+H)+ at m/z 317 in the positive FAB/MS. In the ¹H-NMR spectrum of 1, two olefinic methine signals at δ6.15(1H, d, J = 9.6 Hz, H-1', ddd) and δ6.10(1H, dd), which indicate the presence of a pyran ring by the coupling constant, two oxygenated methine signals at δ4.58(1H, m) and δ4.49(1H, dd), an oxygenated methylene signal at δ4.32(1H, d, J = 9.6 Hz, d, ddd), and two methylene signals at δ2.55(1H, d, ddd), δ2.25 (1H, ddd), δ2.15 (1H, d, ddd), and 2.03 (1H, d, ddd) were observed. The ¹C-NMR spectrum of 1 exhibited eight carbons consisting of two olefinic methine signals at δ133.2 and δ130.6, one oxygenated quaternary signal at δ76.9, two oxygenated methine signals at δ83.4 and δ65.3, one oxygenated methylene signal at δ67.2, and two methylene signals at δ39.8 and δ39.7. To confirm the position of each carbon, 2D-NMRs including gCOSY, gHSQC, and gHMBC were performed. A series of the partial structure was inferred by gCOSY, and the carbon and proton signals were exactly assigned by gHSQC. In addition, based on the spectrum of gHMBC, sites of the functional groups were verified. Through comparison of these NMR data with those in the literature, compound 1 was identified as 1,4-dihydroxy-3,4-(epoxyethano)-5-cyclohexene, previously isolated from *Millingtonia hortensis*.

**Compound 2**, oils, showed absorbance bands due to the hydroxyl (3410 cm⁻¹), carbonyl (1710 cm⁻¹), and olefine (1690 cm⁻¹) in the IR spectrum (MeOH), and molecular ion peak (M+H)+ at m/z 317 in the positive FAB/MS. In the ¹H-NMR spectrum, the partial structure of a para disubstituted benzene was confirmed from the olefine signals at δ7.01(2H, d), δ6.11(2H, d), one hexose was confirmed by an anomeric signal at δ4.21 (1H, d), and several oxygenated methine and methylene signals at δ3.92 - δ3.53. In addition, an oxygenated methylene signal at δ3.99 (1H, d) and δ3.63 (1H, dt) and a methylene signal at δ2.04 (2H, t), which showed the mutual coupling, were observed, thus confirming the existence of an oxygenated ethyl group. In the ¹C-NMR spectrum, 14 signals consisting of a ketone signal at δ178.7 and four olefine methine signals overlapped two by two at δ154.3 and δ127.8 were observed. In addition, one each oxygenated quaternary, oxygenated methylene, and methylene at δ69.2, 65.7, and 41.0, respectively, were observed. By comparing the chemical shifts of the sugar with those in the literature, hexose was determined to be a glucopyranose. Compound 2 was finally identified as a cornoside by comparing the physical and spectral data with those of compounds isolated from *M. hortensis*. Compounds 1 and 2 were isolated for the first time from this plant.

Because the flower of *C. grandiflora* has been used traditionally in Korea for the treatment of diseases related to hematemesis, menopause, and menstrual irregularity, studies on the biological activities related to arteriosclerosis and hyperpiesia, among others, of compounds 1 and 2 should be performed.

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**References**

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