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Phytochemical Constituents of *Allium victorialis* var. *platyphyllum*

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Abstract – Phytochemical investigation of the 80% MeOH extract from the leaves of *Allium victorialis* var. *platyphyllum* resulted in the isolation of seventeen compounds; two terpenes, three norsesquiterpenes, one furofuran lignan, and eleven phenolic derivatives. Their chemical structures were characterized by spectroscopic methods to be *trans*-phytol (**1**), phytene-1,2-diol (**2**), icariside B_2 (**3**), (6*S*,9*S*)-roseoside (**4**), sedumoside G (**5**), pinoresinol-4-*O*-glucoside (**6**), 2-methoxy-2-(4'-hydroxyphenyl)ethanol (**7**), 2-hydroxy-2-(4'-hydroxyphenyl)ethanol (**8**), Benzyl *β*-D-glucopyranoside (**9**), methyl ferulate (**10**), *trans*-ferulic acid (**11**), methyl-*p*-hydroxycinnamate (**12**), glucosyl methyl ferulate (**13**), linocaffein (**14**), siringin (**15**), 2-(4-hydroxy-3-methoxyphenyl)-ethyl-*O*-*β*-D-glucopyranoside (**16**), and pseudolaroside C (**17**). All compounds were isolated for the first time from this plant.
Keywords – *Allium victorialis* var. *platyphyllum*, Liliaceae, Terpene, Norsesquiterpene, Phenolic compound

Introduction

The leaves of *Allium victorialis* var. *platyphyllum* (Liliaceae) are an edible crop and widely distributed throughout the Ullung island and Gang-Won province in Korea. It is traditionally used as a folk medicine for the treatment of gastritis and heart failures (Park *et al*., 2005). There have been several reports on the isolation of flavonoids and steroidal saponins (Lee *et al*., 2001) from this plant, but little phytochemical investigations have been carried out. In the course of our continuing search for biologically active components from Korean medicinal plants, we investigated the constituents of the leaves of *A. victorialis* var. *platyphyllum* and recently reported the isolation of flavonoids and their anti-inflammatory activity (Woo *et al*., 2012). Further chemical investigation of this plant led to isolation of two terpenes (**1 - 2**), three norsesquiterpenes (**3 - 5**), one furofuran lignan (**6**), and eleven phenolic derivatives (**7 - 17**). Their structures were determined by physicochemical and spectroscopic methods. All compounds were isolated for the first time from this plant source.

Experimental

General experimental procedures – TLC was performed using Merck precoated Silica gel F_{254} plates and RP-18 F_{254}s plates. Spots were detected on thin layer chromatography (TLC) under UV light or by heating after spraying with 10% H_2SO_4 in C_2H_5OH (v/v). Packing material of molecular sieve column chromatography was Sephadex LH-20 (Pharmacia Co.). Sep-Pak® (Waters, Vac 6cc) and RediSep® (ISCO, C-18 Reverse Phase 4.3 g) were also used for column chromatography. Low pressure liquid chromatography was carried out over a Merck LiChroprep Lobar®-A Si 60 (240 × 10 mm) or LiChroprep Lobar®-A RP-C_{18} (240 × 10 mm) column with a FMI QSY-0 pump (ISCO). Preparative HPLC used a Wellchrom K1001 A pump with a Knauer Dual Detector and an Apollo Silica 5*u* column (250 × 22 mm) or Econosil® RP-C_{18} 10*u* column (250 × 22 mm). Silica gel 60 (Merck, 70 - 230 mesh and 230 - 400 mesh) was used for column chromatography. NMR spectra were recorded on a Varian UNITY INOVA 500 NMR spectrometer operating at 500 MHz (^{1}H) and 125 MHz (^{13}C), with chemical shifts given in ppm (δ) using TMS as an internal standard. FAB and EI mass spectra were obtained on a JEOL JMS 700 mass spectrometer.

Plant materials – The leaves of *A. victorialis* var. *platyphyllum* were collected in Taeback, Gangwon province, Korea in January, 2011, and the plant was identified by one of the authors (K.R. Lee). A voucher specimen (SKKU-NPL 1105) was deposited in the herbarium of the School of Pharmacy, Sungkyunkwan University, Suwon, Korea.

Extraction and isolation – The half dried leaves of *A.*

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victorialis var. *platyphyllum* (2.7 kg) were extracted with 80% MeOH three times at room temperature and evaporated under reduced pressure to give a residue (314.0 g), which was dissolved in water (800 ml) and partitioned with solvent to give *n*-hexane (17.0 g), $CHCl_3$ (2.2 g), EtOAc (3.4 g), and *n*-BuOH (50.0 g) soluble portions. The hexane fraction (17.0 g) was separated over a silica gel column ($CHCl_3$: MeOH = 80 : 1 – 1 : 1) to yield eight fractions (H1 – H8). Fraction H1 (4.5 g) was separated over a silica gel column (hexane : EtOAc = 8 : 1 – 1 : 1) to yield twelve fractions (H1-1 – H1-12). Subfraction H1-5 (600 mg) was separated over an RP-C_{18} silica gel column with 85% MeOH and further purified over a silica gel prep. HPLC (hexane : EtOAc = 5 : 1) to afford compound **1** (53 mg, R_t = 13.0 min). Subfraction H1-9 (80 mg) was separated over an RP-C_{18} silica Lobar A®-column (80% MeOH) and purified over a silica gel prep. HPLC (hexane : $CHCl_3$: MeOH = 10 : 30 : 0.1) to yield compound **10** (10 mg, R_t = 12.5 min). Subfraction H1-11 (80 mg) separated over an silica Lobar A®-column (hexane : EtOAc = 4 : 1) and purified over a silica gel prep. HPLC (hexane : $CHCl_3$: MeOH = 5 : 30 : 0.5) to yield compound **2** (13 mg, R_t = 12.5 min). The chloroform fraction (2.2 g) was separated over a silica gel column ($CHCl_3$: MeOH = 80 : 1 – 1 : 1) to yield eighteen fractions (C1 – C18). Fraction C4 (80 mg) was purified with a silica Lobar A®-column (hexane : EtOAc = 1 : 1) and silica gel prep. HPLC (hexane : EtOAc = 7 : 1) to afford compound **12** (5 mg, R_t = 11.0 min). Fraction C9 (180 mg) was separated over a Sephadex LH-20 column (90% MeOH) to yield five subfractions (C9-1 – C9-5). Subfraction C9-3 (16 mg) was purified with Sep-Pak® (50% MeOH) to yield compound **7** (7 mg). Subfraction C9-5 (11 mg) was purified with an RP-C_{18} prep. HPLC (50% MeOH) to afford compound **11** (4 mg, R_t = 12.0 min). Fraction C13 (130 mg) was separated over a Sephadex LH-20 column (90% MeOH) and further purified with an RP-C_{18} prep. HPLC (50% MeOH) to yield compound **6** (3 mg, R_t = 10.0 min). The ethyl acetate fraction (3.4 g) was separated over a silica gel column ($CHCl_3$: MeOH = 25 : 1 – 1 : 1) to yield twelve fractions (E1 – E12). Fraction E8 (150 mg) was separated over an RP-C_{18} silica Lobar A®-column (50% MeOH) to afford five subfractions (E8-1 – E8-5). Subfraction E8-1 (50 mg) was separated over a Sephadex LH-20 column (90% MeOH) and further purified with RediSep® (100% EtOAc) to afford compound **8** (7 mg). Fraction E9 (260 mg) was separated over an RP-C_{18} silica Lobar A®-column (45% MeOH) to afford six subfractions (E9-1 – E9-6). Subfraction E9-2 (14 mg) was purified with an RP-C_{18} prep. HPLC (35% MeOH) to afford compound **17** (3 mg, R_t = 16.0 min). Subfraction E9-3 (30 mg) was purified with an RP-C_{18} prep. HPLC (25% MeCN) to yield compound **9** (3 mg, R_t = 9.0 min) and compound **3** (13 mg, R_t = 12.0 min). Subfraction E9-4 (50 mg) was purified over a silica gel prep. HPLC ($CHCl_3$: MeOH = 20 : 1) to afford compound **13** (4 mg, R_t = 23.0 min). Fraction E10 (300 mg) was separated over an RP-C_{18} silica gel column with 40% MeOH as the eluent to give five subfractions (E10-1 – E10-5). Subfraction E10-1 (88 mg) was separated over a Sephadex LH-20 column (90% MeOH) and further purified with an RP-C_{18} prep. HPLC (30% MeOH) to afford compound **14** (3 mg, R_t = 31.0 min). Subfraction E10-2 (95 mg) separated over an silica Lobar A®-column ($CHCl_3$: MeOH = 13 : 1) and purified with an RP-C_{18} prep. HPLC (30% MeOH) to afford compound **4** (10 mg, R_t = 21.0 min). The butanol fraction (50.0 g) was chromatographed on a Diaion HP-20 column eluted with a gradient solvent system consisting of 100% H_2O and 100% MeOH. This yielded two subfractions A and B. Fraction A (10.0 g) was separated over a silica gel column ($CHCl_3$: MeOH : H_2O = 7 : 1 : 0.1 – 1 : 1 : 1) to yield twelve fractions (A1 – A12). Fraction A5 (510 mg) was separated over an RP-C_{18} silica gel column with 35% MeOH as the eluent to give six subfractions (A5-1 – A5-6). Subfraction A5-2 (60 mg) was purified with an RP-C_{18} prep. HPLC (30% MeOH) to afford compounds **15** (8 mg, R_t = 16.0 min) and **16** (4 mg, R_t = 14.0 min). Subfraction A5-5 (60 mg) was purified with an RP-C_{18} prep. HPLC (45% MeOH) to afford compound **5** (5 mg, R_t = 20.0 min).

***trans*-Phytol** (**1**) – Coloress oil; FAB-MS *m/z* : 319 $[M + Na]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 5.35 (1H, t, *J* = 7.0 Hz, H-2), 4.07 (2H, d, *J* = 6.5 Hz, H-1), 2.00 (2H, t, *J* = 6.5 Hz, H-4), 1.65 (3H, s, H-20), 1.52 - 1.05 (19H, m), 0.87 (9H, d, *J* = 6.5 Hz, H-16, 18, 19), 0.88 (3H, d, *J* = 6.5 Hz, H-17); ^{13}C NMR (125 MHz, CD_3OD): δ 138.4 (C-3), 123.6 (C-2), 58.2 (C-1), 39.8 (C-4), 39.4 (C-14), 37.4 (C-8), 37.3 (C-10), 37.2 (C-12), 36.6 (C-6), 32.8 (C-7), 32.7 (C-11), 27.9 (C-15), 25.1 (C-5), 24.7 (C-13), 24.3 (C-9), 22.0 (C-17), 21.9 (C-16), 19.1 (C-19), 19.0 (C-18), 15.0 (C-20).

Phytene-1,2-diol (**2**) – Coloress gum; EI-MS m/z : 312 $[M]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 5.07 (1H, s, H-20a), 4.89 (1H, s, H-20b), 4.07 (1H, dd, *J* = 7.0, 3.5 Hz, H-2), 3.58 (1H, dd, *J* = 6.5, 4.0 Hz, H-1a), 3.44 (1H, dd, *J* = 6.5, 2.5 Hz, H-1b), 2.09 - 1.97 (2H, m, H-4), 1.57-1.06 (19H, m), 0.88 (9H, d, *J* = 7.0 Hz, H-16, 18, 20), 0.86 (3H, d, *J* = 7.0 Hz, H-19); ^{13}C NMR (125 MHz, CD_3OD): δ 149.6 (C-3), 109.6 (C-17), 75.4 (C-2), 65.3 (C-1), 39.3 (C-14), 37.3 (C-8), 37.2 (C-10, 12), 36.8 (C-6), 32.7 (C-4),

32.5 (C-7, 11), 27.9 (C-15), 25.5 (C-5), 24.6 (C-13), 24.3 (C-9), 21.9 (C-20), 21.8 (C-16), 19.0 (C-19), 18.9 (C-18).

Icariside B_2 (**3**) – Coloress gum; EI-MS *m/z* : 386 $[M]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 7.16 (1H, d, *J* = 16.0 Hz, H-7), 6.18 (1H, d, *J* = 16.5 Hz, H-8), 4.33 (1H, d, *J* = 8.0 Hz, H-1'), 3.92 (1H, m, H-3), 3.86 - 3.10 (5H, m, sugar-H), 2.38 (1H, dd, *J* = 15.0, 3.5 Hz, H-4a), 2.28 (3H, s, H-10), 1.81 (1H, dd, *J* = 14.5, 8.5 Hz, H-2a), 1.73 (1H, dd, *J* = 11.5, 2.0 Hz, H-4b), 1.41 (1H, dd, *J* = 12.5, 10.0 Hz, H-2b), 1.21 (3H, s, H-13), 1.18 (3H, s, H-12), 0.95 (3H, s, H-11); ^{13}C NMR (125 MHz, CD_3OD): δ 199.0 (C-9), 144.0 (C-7), 132.6 (C-8), 101.7 (C-1'), 76.9 (C-3'), 76.6 (C-3'), 73.9 (C-2'), 71.5 (C-3), 70.4 (C-4'), 69.9 (C-6), 67.1 (C-5), 61.5 (C-6'), 44.0 (C-2), 36.9 (C-4), 34.7 (C-1), 28.2 (C-11), 26.2 (C-10), 24.3 (C-12), 19.0 (C-13).

(6*S*,9*S*)-Roseoside (**4**) – Coloress gum; $[\alpha]_D^{25}$: +57.7° (c 0.06, MeOH); EI-MS *m/z* : 386 $[M]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 5.96 (1H, d, *J* = 16.0 Hz, H-7), 5.86 (1H, s, H-4), 5.72 (1H, dd, *J* = 15.5, 7.0 Hz, H-8), 4.52 (1H, m, H-9), 4.27 (1H, d, *J* = 8.5 Hz, H-1'), 3.84 (1H, dd, *J* = 12.0, 2.5 Hz, H-6a'), 3.63 (1H, dd, *J* = 12.0, 6.0 Hz, H-6b'), 3.26 - 3.13 (4H, m, sugar-H), 2.60 (1H, d, *J* = 17.0 Hz, H-2a), 2.17 (1H, d, *J* = 16.5 Hz, H-2b), 1.94 (3H, s, H-13), 1.28 (3H, d, *J* = 6.5 Hz, H-10), 1.04 (1H, s, H-11), 1.01 (1H, s, H-12); ^{13}C NMR (125 MHz, CD_3OD): δ 200.0 (C-3), 165.9 (C-5), 132.5 (C-7), 125.9 (C-4), 100.0 (C-1'), 78.8 (C-6), 77.1 (C-3'), 77.0 (C-5'), 73.7 (C-9), 73.4 (C-2'), 70.4 (C-4'), 61.6 (C-6'), 49.5 (C-2), 41.2 (C-1), 23.5 (C-12), 22.3 (C-11), 21.0 (C-10), 18.3 (C-13).

Sedumoside G (**5**) – Coloress gum; FAB-MS *m/z* : 543 $[M + Na]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 4.73 (1H, s, H-1"), 4.32 (1H, d, *J* = 7.5 Hz, H-1'), 3.95 (1H, dd, *J* = 10.0, 1.5 Hz, H-6'), 3.75 (1H, m, H-3), 3.80 - 3.11 (9H, m, sugar-H), 2.59 (1H, m, H-8a), 2.46 (1H, m, H-8b), 2.12 (3H, m, H-10), 2.05 (1H, m, H-4a), 1.79 (1H, m, H-2a), 1.69 (1H, m, H-7a), 1.45 (1H, m, H-7b), 1.26 (1H, d, *J* = 6.0 Hz, H-6"), 1.14 (1H, m, H-2b), 1.05 (1H, m, H-4b), 0.97 (3H, s, H-13), 0.95 (3H, s, H-12), 0.84 (3H, s, H-11), 0.59 (1H, m, H-6); ^{13}C NMR (125 MHz, CD_3OD): δ 210.4 (C-9), 101.6 (C-1'), 100.7 (C-1"), 76.6 (C-3'), 75.2 (C-5'), 74.7 (C-3), 73.7 (C-2'), 72.6 (C-4"), 70.9 (C-3"), 70.8 (C-2"), 70.3 (C-4'), 68.3 (C-5"), 66.6 (C-6'), 52.0 (C-6), 47.1 (C-2), 44.9 (C-9), 43.4 (C-4), 35.2 (C-1), 33.4 (C-5), 29.8 (C-12), 28.4 (C-10), 22.5 (C-7), 20.0 (C-13), 19.8 (C-11), 16.7 (C-6").

Pinoresinol-4-*O*-glucoside (**6**) – Coloress gum; FAB-MS *m/z* : 543 $[M + Na]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 7.14 (1H, d, *J* = 8.5 Hz, H-5), 7.02 (1H, d, *J* = 2.0 Hz, H-2), 6.94 (1H, d, *J* = 2.0 Hz, H-2'), 6.91 (1H, dd, *J* = 8.5, 2.0 Hz, H-6), 6.81 (1H, dd, *J* = 8.0, 2.0 Hz, H-6'), 6.76 (1H, d, *J* = 8.0 Hz, H-5'), 4.87 (2H, d, *J* = 7.5 Hz, H-1"), 4.74 (1H, d, *J* = 4.0 Hz, H-7), 4.69 (1H, d, *J* = 4.5 Hz, H-7'), 4.24 (2H, m, H-9a, 9'a), 3.87 (3H, s, 3-OCH_3), 3.85 (3H, s, 3'-OCH_3), 3.82 (2H, m, H-9b, 9'b), 3.70 - 3.26 (5H, m, sugar-H), 3.12 (2H, m, H-8, 8'); ^{13}C NMR (125 MHz, CD_3OD): δ 149.8 (C-4), 147.9 (C-4'), 146.3 (C-3'), 146.1 (C-3), 136.3 (C-1), 132.5 (C-1'), 118.8 (C-6'), 118.6 (C-6), 116.8 (C-5), 114.9 (C-5'), 110.4 (C-2), 109.8 (C-2'), 101.6 (C-1"), 86.3 (C-7'), 85.9 (C-7), 77.0 (C-5"), 76.7 (C-3"), 73.9 (C-2"), 71.5 (C-9'), 71.4 (C-9), 70.4 (C-4"), 61.5 (C-6"), 55.5 (3-OCH_3), 55.2 (3'-OCH_3), 54.3 (C-8'), 54.1 (C-8).

2-Methoxy-2-(4'-hydroxyphenyl)ethanol (**7**) – Coloress gum; EI-MS *m/z* : 168 $[M]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 7.12 (2H, td, *J* = 8.5, 2.0 Hz, H-2, 6), 6.76 (2H, td, *J* = 9.0, 2.5 Hz, H-3, 5), 4.15 (1H, dd, *J* = 8.0, 4.0 Hz, H-7), 3.61 (1H, dd, *J* = 10.5, 6.5 Hz, H-8a), 3.47 (1H, dd, *J* = 10.5, 4.0 Hz, H-8b), 3.22 (3H, s, 7-OCH_3); ^{13}C NMR (125 MHz, CD_3OD): δ 157.0 (C-4), 129.4 (C-1), 127.9 (C-2, 6), 114.8 (C-3, 5), 84.5 (C-7), 66.3 (C-8), 55.4 (7-OCH_3).

2-Hydroxy-2-(4'-hydroxyphenyl)ethanol (**8**) – Coloress gum; EI-MS *m/z* : 154 $[M]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 7.17 (2H, td, *J* = 8.0, 2.0 Hz, H-2, 6), 6.75 (2H, td, *J* = 8.5, 2.0 Hz, H-3, 5), 4.58 (1H, t, *J* = 7.0 Hz, H-7), 3.58 (2H, brd, *J* = 7.0 Hz, H-8); ^{13}C NMR (125 MHz, CD_3OD): δ 158.0 (C-4), 134.1 (C-1), 128.7 (C-2, 6), 116.8 (C-3, 5), 75.5 (C-7), 68.7 (C-8).

Benzyl β-D-glucopyranoside (**9**) – Coloress gum; FAB-MS *m/z* : 271 $[M + H]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 7.42 (2H, m, H-3, 5), 7.33 (2H, m, H-2, 6), 7.26 (1H, m, H-4), 4.92 (1H, d, *J* = 12.0 Hz, H-7a), 4.66 (1H, d, *J* = 12.0 Hz, H-7b), 4.35 (1H, d, *J* = 7.0 Hz, H-1'), 3.89 (1H, dd, *J* = 11.5, 2.0 Hz, H-6a'), 3.68 (1H, dd, *J* = 11.5, 5.5 Hz, H-6b'), 3.35-3.22 (4H, m, sugar-H); ^{13}C NMR (125 MHz, CD_3OD): δ 137.6 (C-1), 127.9 (C-3, 5), 127.8 (C-2, 6), 127.3 (C-4), 101.8 (C-1'), 76.7 (C-3'), 76.6 (C-5'), 73.7 (C-2'), 70.3 (C-7), 70.2 (C-4'), 61.4 (C-6').

Methyl ferulate (**10**) – Coloress gum; EI-MS *m/z* : 208 $[M]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 7.60 (1H, d, *J* = 16.0 Hz, H-7), 7.17 (1H, d, *J* = 2.0 Hz, H-2), 7.05 (1H, dd, *J* = 8.0, 2.0 Hz, H-6), 6.80 (1H, d, *J* = 8.0 Hz, H-5), 6.35 (1H, d, *J* = 15.5 Hz, H-8), 3.90 (3H, s, 3-OCH_3), 3.75 (3H, s, $COOCH_3$); ^{13}C NMR (125 MHz, CD_3OD): δ 168.5 (C-9), 149.4 (C-4), 148.2 (C-3), 145.6 (C-7), 126.5 (C-1), 122.8 (C-6), 115.3 (C-5), 114.0 (C-8), 110.5 (C-2), 55.2 (3-OCH_3), 50.8 ($COOCH_3$).

***trans*-Ferulic acid** (**11**) – Coloress gum; EI-MS *m/z* : 194 $[M]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 7.57 (1H, d,

J = 16.5 Hz, H-7), 7.17 (1H, d, J = 2.0 Hz, H-2), 7.05 (1H, dd, J = 8.5, 2.0 Hz, H-6), 6.80 (1H, d, J = 8.0 Hz, H-5), 3.89 (3H, s, 3-OCH_3); ^{13}C NMR (125 MHz, CD_3OD): δ 169.9 (C-9), 148.9 (C-3), 147.9 (C-7), 145.6 (C-4), 126.5 (C-1), 122.4 (C-6), 115.0 (C-5, 8), 110.2 (C-2), 55.0 (3-OCH_3).

Methyl-*p*-hydroxycinnamate (**12**) – Coloress gum; FAB-MS m/z : 179 $[M+H]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 7.60 (1H, d, J = 16.0 Hz, H-7), 7.44 (1H, d, J = 8.5 Hz, H-2, 6), 6.79 (1H, d, J = 9.0 Hz, H-3, 5), 6.31 (1H, d, J = 16.0 Hz, H-8), 3.75 (3H, s, 3-OCH_3); ^{13}C NMR (125 MHz, CD_3OD): δ 168.6 (C-9), 160.1 (C-4), 145.4 (C-7), 129.9 (C-2, 6), 126.5 (C-1), 115.7 (C-3, 5), 114.7 (C-8), 50.8 (3-OCH_3).

Glucosyl methyl ferulate (**13**) – Coloress gum; EI-MS m/z : 370 $[M]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 7.63 (1H, d, J = 16.0 Hz, H-7), 7.25 (1H, brs, H-2), 7.17 (1H, d, J = 8.0 Hz, H-5), 7.15 (1H, dd, J = 8.5, 2.5 Hz, H-6), 6.44 (1H, d, J = 16.5 Hz, H-8), 4.96 (1H, d, J = 7.5 Hz, H-1'), 3.89 (3H, s, 3-OCH_3), 3.77 (3H, s, $COOCH_3$), 3.88-3.27 (5H, m, sugar-H); ^{13}C NMR (125 MHz, CD_3OD): δ 168.7 (C-9), 150.5 (C-3), 149.9 (C-4), 145.6 (C-6), 129.8 (C-1), 123.2 (C-6), 117.8 (C-5), 117.2 (C-8), 112.3 (C-2), 101.2 (C-1'), 77.1 (C-3'), 76.5 (C-5'), 74.3 (C-2'), 70.2 (C-4'), 61.3 (C-6'), 55.8 (3-OCH_3), 52.1 ($COOCH_3$)

Linocaffein (**14**) – Coloress gum; EI-MS m/z : 356 $[M]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 7.57 (1H, d, J = 16.0 Hz, H-7), 7.20 (1H, d, J = 8.5 Hz, H-5), 7.10 (1H, d, J = 2.0 Hz, H-2), 7.04 (1H, dd, J = 8.5, 1.5 Hz, H-6), 6.36 (1H, d, J = 16.0 Hz, H-8), 4.84 (1H, d, J = 7.5 Hz, H-1'), 3.90 (1H, dd, J = 12.0, 2.0 Hz, H-6a), 3.76 (3H, s, $COOCH_3$), 3.71 (1H, dd, J = 12.0, 5.0 Hz, H-6b), 3.35 - 3.26 (4H, m, sugar-H); ^{13}C NMR (125 MHz, CD_3OD): δ 169.4 (C-9), 149.1 (C-4), 148.8 (C-3), 146.2 (C-7), 131.2 (C-1), 122.2 (C-6), 118.2 (C-5), 116.0 (C-2), 103.6 (C-1'), 78.5 (C-3'), 77.7 (C-5'), 74.9 (C-2'), 71.4 (C-4'), 62.5 (C-6'), 52.2 ($COOCH_3$)

Siringin (**15**) – Coloress gum; EI-MS m/z : 372 $[M]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 6.75 (2H, s, H-2, 6), 6.54 (1H, d, J = 16.0 Hz, H-7), 6.33 (1H, dd, J = 15.5, 6.0 Hz, H-8), 4.86 (1H, d, J = 7.0 Hz, H-1'), 4.22 (1H, dd, J = 5.5, 1.5 Hz, H-9), 3.85 (6H, s, 3, 5-OCH_3), 3.84 - 3.19 (5H, m, sugar-H); ^{13}C NMR (125 MHz, CD_3OD): δ 153.1 (C-3, 5), 134.0 (C-4), 130.0 (C-1, 7), 128.8 (C-8), 104.2 (C-2, 6), 104.1 (C-1'), 77.1 (C-3'), 76.6 (C-5'), 74.5 (C-2'), 70.1 (C-4'), 62.3 (C-9), 61.4 (C-6'), 55.8 (3, 5-OCH_3).

2-(4-Hydroxy-3-methoxyphenyl)-ethyl-*O*-*β*-D-glucopyranoside (**16**) – Coloress gum; FAB-MS m/z : 331 $[M+H]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 6.85 (1H, d, J = 1.5 Hz, H-2), 6.67 (1H, dd, J = 8.0, 1.5 Hz, H-6), 6.66 (1H, d, J = 8.5 Hz, H-5), 4.29 (1H, d, J = 8.0 Hz, H-1'), 4.06 (1H, m, H-8a), 3.86 (1H, dd, J = 12.5, 2.0 Hz, H-6a), 3.83 (3H, s, 3-OCH_3), 3.71 (1H, m, H-8b), 3.66 (1H, dd, J = 12.0, 5.5 Hz, H-6b), 3.36 - 3.16 (4H, m, sugar-H), 2.84 (2H, t, J = 7.5 Hz, H-7); ^{13}C NMR (125 MHz, CD_3OD): δ 147.6 (C-3), 144.7 (C-4), 130.4 (C-1), 121.2 (C-6), 114.8 (C-5), 112.6 (C-2), 103.1 (C-1'), 76.9 (C-3'), 76.7 (C-5'), 73.9 (C-2'), 70.7 (C-8), 70.5 (C-4'), 61.6 (C-6'), 55.2 (3-OCH_3), 35.5 (C-7).

Pseudolaroside C (**17**) – Coloress gum; EI-MS m/z : 314 $[M]^+$; ^{1}H NMR (500 MHz, CD_3OD): δ 7.96 (2H, dd, J = 7.0, 2.5 Hz, H-2, 6), 7.14 (2H, dd, J = 7.0, 2.5 Hz, H-3, 5), 5.00 (1H, d, J = 7.0 Hz, H-1'), 3.99 (1H, dd, J = 12.0, 2.0 Hz, H-6a'), 3.87 (3H, s, $COOCH_3$), 3.69 (1H, dd, J = 12.0, 5.5 Hz, H-6b'), 3.50 - 3.28 (4H, m, sugar-H); ^{13}C NMR (125 MHz, CD_3OD): δ 167.0 (C-7), 161.7 (C-4), 131.2 (C-2, 6), 123.9 (C-1), 116.0 (C-3, 5), 100.5 (C-1'), 77.0 (C-3'), 76.8 (C-5'), 73.6 (C-2'), 70.1 (C-4'), 61.6 (C-6'), 51.2 ($COOCH_3$).

Results and Discussion

Column chromatographic separation of the 80% methanol extract from the leaves of *A. victorialis* var. *platyphyllum* led to the isolation of two terpenes, three norsesquiterpenes, one furofuran lignan, and eleven phenolic derivatives. Compounds **1** - **13** and **15** - **17** were identified by comparing the ^{1}H-, ^{13}C-NMR, and MS spectral data with the literature values to be *trans*-phytol (**1**) (Kim *et al*., 2008), phytene-1,2-diol (**2**) (Lee and Lee, 2005), icariside B_2 (**3**) (Kim *et al*., 2009), (6*S*,9*S*)-roseoside (**4**) (Kim *et al*., 2008), sedumoside G (**5**) (Morikawa *et al*., 2007), pinoresinol-4-*O*-glucoside (**6**) (Kim *et al*., 2005), 2-methoxy-2-(4'-hydroxyphenyl)ethanol (**7**), 2-hydroxy-2-(4'-hydroxyphenyl)ethanol (**8**) (Kim *et al*., 2006), benzyl *β*-D-glucopyranoside (**9**) (Kim *et al*., 2008), methyl ferulate (**10**) (Choi *et al*., 2004), *trans*-ferulic acid (**11**) (Park *et al*., 2009), methyl-*p*-hydroxycinnamate (**12**) (Lee *et al*., 2009), glucosyl methyl ferulate (**13**) (Shimomura *et al*., 1988), siringin (**15**) (Greca *et al*., 1998), 2-(4-hydroxy-3-methoxyphenyl)-ethyl-*O*-*β*-D-gluco pyranoside (**16**) (Marino *et al*., 2004) and pseudolaroside C (**17**) (Feng *et al*., 2008) (Fig. 1). All compounds were isolated for the first time from this plant source.

The following describes the structure elucidation of compound **14**, which was synthesized (Klosterman and Muggli, 1959) and has been isolated from *Ranunculus ternatus* (Tian *et al*., 2007) and *Equisetum myriochaetum* (Wiedenfeld *et al*., 2000), but NMR spectral data were not yet reported.

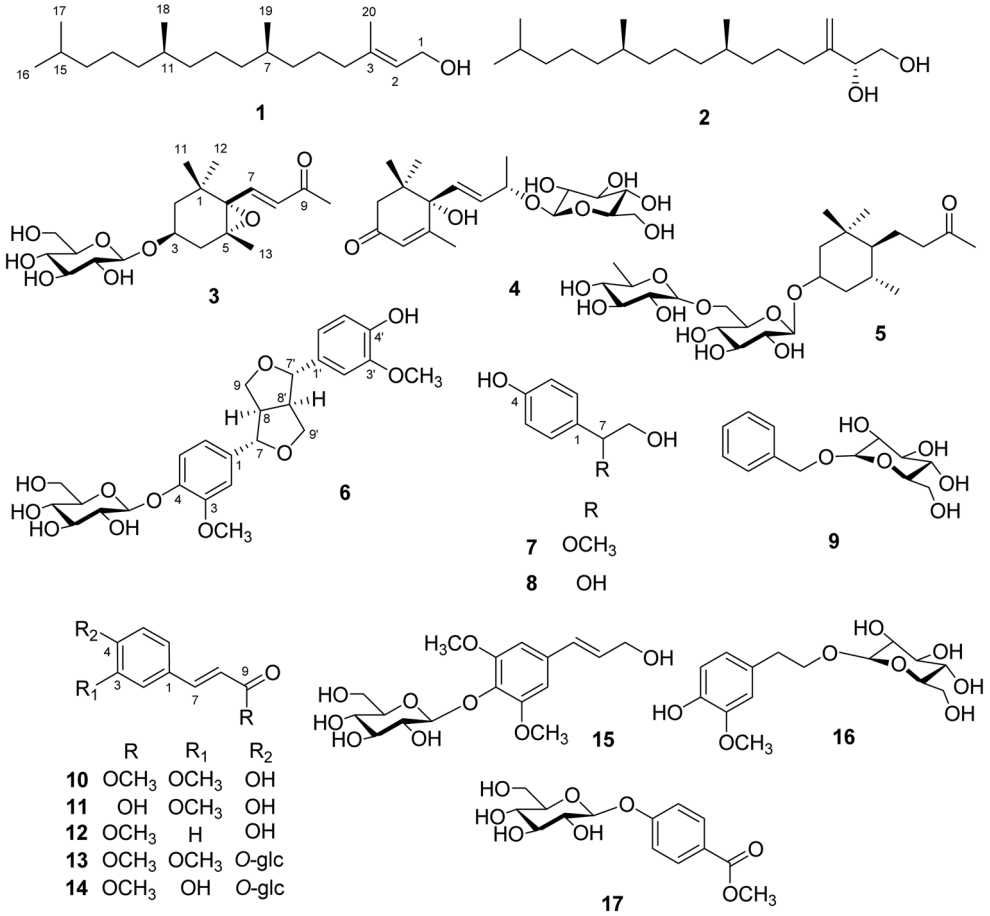

Fig. 1. The structures of **1** - **17** from *A. victorialis* var. *platyphyllum.*

Compound **14** was obtained yellowish gum. The EI-MS (*m/z* 356 $[M]^+$) and ^{1}H-, ^{13}C-NMR spectral data of **14** afforded a molecular formula of $C_{16}H_{20}O_9$. The ^{1}H-NMR spectrum showed three aromatic protons at δ 7.20 (1H, d, J = 8.5 Hz), 7.10 (1H, d, J = 2.0 Hz), and 7.04 (1H, dd, J = 8.5, 1.5 Hz), two olefinic proton signals at 7.57 (1H, d, J = 16.0 Hz) and 6.36 (1H, d, J = 16.0 Hz), one methoxy group at 3.76 (3H, s). The ^{13}C-NMR spectrum exhibited 10 carbon resonances, consisting of an ester carbonyl signal at δ 169.4, two olefinic carbon signals at δ 146.2 and 118.2, one methoxy carbon at δ 52.2 and 6 aromatic carbon signals at δ 149.1, 148.8, 131.2, 122.2, 118.2, and 116.0. These spectral data suggested that **14** was a phenylpropanoid derivative (Park *et al*., 2009). In addition, glucose signals [δ 4.84 (1H, d, J = 7.5 Hz), 3.90 (1H, dd, J = 12.0 , 2.0 Hz) 3.71 (1H, dd, J = 12.0, 5.0 Hz), and 3.35 - 3.26 (4H, m); δ 103.6, 78.5, 77.7, 74.9, 71.4, and 62.5] were displayed. The J value of the anomeric proton of D-glucose indicated that it was β form (Stephen *et al*, 1977). The location of D-glucose was established by an HMBC experiment, in which a long-range correlation was observed between H-1' (δ 4.84) and C-4 (δ 149.1) (Fig. 2). Based on the above evidences, the structure of **14** was determined to be linocaffein.

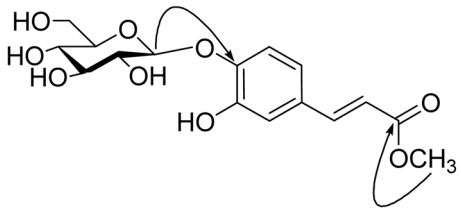

Fig. 2. Key HMBC (→) correlations of **14**.

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