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Chemical Constituents from the Aerial Parts of *Aster yomena*

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Abstract – Nine terpenoids, spinasterone (**1**), simiarenol (**2**), phytol (**3**), lupeol (**4**), α-amyrin (**5**), 1*β*,4*β*-dihydroxyeudesman-11-ene (**6**), 3,7-dihydroxyhumula-4,8(15),10(*E*)-triene (**7**), 2,6-dihydroxyhumula-3(12),7(13),9*E*-triene (**8**), 23-hydroxybetulin (**9**) were isolated from the aerial parts of *Aster yomena* M. Their structures were identified based on 1D and 2D NMR, including ^{1}H-^{1}H COSY, HSQC, HMBC and NOESY spectroscopic analyses. Compounds **1 - 9** were isolated from this plant for the first time.
Key words – *Aster yomena*, Asteraceae, Terpenoids

Introduction

Aster yomena Makino (Asteraceae), a perennial herb that grows mainly in southern part of Korea, has been used in traditional medicines for the treatment of bronchial asthma, inflammation, and cold (Lee 1993; Ahn 1998). Previous phytochemical studies on this plant have not been nearly done. Recently, we have reported a new megastigmane palmitate, 5(13)-megastigmene-9-one-2*β*-palmitate, and a new oleanane triterpenoid, 3*β*,23,28-trihydroxy-12-oleanene-11-one, together with three known oleanane-type triterpenoids, *β*-amyrin, erythrodiol, and 3*β*,23,28-triol olean-12-ene from the methylene chloride soluble fraction of this plant (Jin *et al*., 2012).

In our continuing studies on this plant, nine terpenoids, spinasterone (**1**), simiarenol (**2**), phytol (**3**), lupeol (**4**), α-amyrin (**5**), 1*β*,4*β*-dihydroxyeudesman-11-ene (**6**), 3,7-dihydroxyhumula-4,8(15),10(*E*)-triene (**7**), 2,6-dihydroxy humula-3(12),7(13),9*E*-triene (**8**) and 23-hydroxybetulin (**9**) were isolated. All isolates have not yet been reported from this plant.

Experimental

General experimental procedures – The optical rotations were measured using an Autopol-IV polarimeter (Rudolph Research Flangers). The EI-MS spectra was recorded on a JEOL JMS 700 mass spectrometer. The NMR spectra were recorded on a JEOL 300, Varian Unity Inova 500 and Unity Inova 600 spectrometer (KBSI-Gwangju center). Semi-preparative HPLC was performed using a Waters HPLC system equipped with Waters 600 Q-pumps, a 996 photodiode array detector, and a YMC-Pack ODS-A column (250 × 10 mm i.d., 5 μm), flow rate 4.0 mL/min. TLC and column chromatography were performed on precoated Si Gel F_{254} plates (Merck, art. 5715), RP-18 F_{254} plates (Merck, art. 15389) and silica gel 60 (40 - 63 and 63 - 200 μm, Merck), MCI gel CHP20P (75 - 150 μm, Mitsubishi Chemical Co.), Sephadex LH-20 (25 - 100 μm, Sigma), LiChroprep RP-18 (40 - 63 μm, Merck).

Plant material – The aerial parts of *Aster yomena* Makino (Asteraceae) were collected from the Herbarium of the College of Pharmacy, Chosun University, Korea, in September 2003 and identified by Prof. E.-R. Woo, one of authors of this paper. A voucher specimen was deposited in the Herbarium of the College of Pharmacy, Chosun University (CSU-1029-17).

Extraction and Isolation – The air-dried aerial parts of *A. yomena* (1.9 kg) were extracted with MeOH three times at room temperature, and 120 g of residue were produced. The MeOH extract was suspended in H_2O and partitioned sequentially in CH_2Cl_2, EtOAc, and *n*-BuOH. The CH_2Cl_2 fraction (15 g) was chromatographed over a silica gel column using a gradient solvent system of hexane:acetone (100 : 1 → 1 : 1) to yield twelve subfractions D1~D12. The D3 fraction (320 mg) was chromatographed over a silica gel column using a gradient solvent system of hexane:acetone (30 : 1 → 1 : 1) to yield three subfractions D31~D33. Subfraction D31 (42 mg) was subjected to RP-18 CC eluting with 99% MeOH to yield six subfractions, D311~D316. D314 and D315 (15.2 mg)

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were purified by silica gel CC (hexane : EtOAc = 2 : 1) to yield compound **1** (1.7 mg) and compound **2** (4.3 mg), respectively. The D5 fraction (800 mg) was chromatographed over a silica gel column using a gradient solvent system of hexane : acetone (10 : 1 → 1 : 1) to yield three subfractions D51~D53. Subfraction D52 (286 mg) was subjected to RP-18 CC eluting with 99% MeOH to yield eight subfractions, D521~D528. D523, D524 and D528 (110 mg) were purified by silica gel CC (hexane : aceton = 10 : 1) to yield compound **3** (4.8 mg), compound **4** (73 mg) and compound **5** (6 mg), respectively. Subfraction D10 (1.7 g) was subjected to RP-18 CC eluting with 100% MeOH to yield four subfractions, D101~D104. Subfraction D101 (850 mg) was subjected to silica gel CC eluting with a gradient solvent system of $CHCl_3$: MeOH (100 : 1 → 100% MeOH) to yield four subfractions, D1011~D1014. D1013 (160 mg) was purified by RP-18 CC (80% MeOH) to yield compound **6** (1.9 mg). Subfraction D11 (2.5 g) was subjected to YMC Sep-Pack eluting with 50% MeOH, 80% MeOH, 100% MeOH to yield three subfractions, D111~D113. Subfraction D112 (900 mg) was subjected to RP-18 CC eluting with 50% MeOH to yield four subfractions, D1121~D1124. D1124 (158 mg) was purified by silica gel CC (hexane : EtOAc = 10 : 1) and Semi-prep HPLC (60% MeOH) to yield compound **7** (1.5 mg) and compound **8** (1.9 mg). Subfraction D113 (900 mg) was subjected to silica gel CC eluting with a gradient solvent system of $CHCl_3$: MeOH (30 : 1 → 100% MeOH) to yield six subfractions, D1131~D1136. Subfraction D1132 (581 mg) was subjected to RP-18 CC eluting with 90% MeOH to yield four subfractions, D11321~D11324. D11323 (80 mg) was purified by Semi-prep HPLC (80% MeOH) to yield compound **9** (6.2 mg).

Spinasterone (1) – White powder; $[\alpha]_D^{25}$: +23° ($CHCl_3$, c = 0.05); EI-MS *m/z*: 410 [M^+]; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.18 (1H, br s, H-7), 5.16 (1H, dd, J = 8.5, 15.2 Hz, H-22), 5.03 (1H, dd, J = 8.8, 15.3 Hz, H-23), 1.04 (3H, d, J = 6.7 Hz, Me-21), 1.02 (3H, s, Me-19), 0.85 (3H, d, J = 6.7 Hz, Me-26), 0.81 (3H, t, J = 7.3 Hz, Me-29), 0.80 (3H, d, J = 6.7 Hz, Me-27), 0.58 (3H, s, Me-18). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 212.1 (s, C-3), 139.5 (s, C-8), 138.1 (d, C-22), 129.5 (d, C-23), 117.0 (d, C-7), 55.8 (d, C-17), 55.0 (t, C-14), 51.2 (d, C-24), 48.8 (d, C-9), 44.2 (t, C-4), 43.2 (s, C-13), 42.8 (d, C-5), 40.8 (d, C-20), 39.3 (t, C-12), 38.7 (t, C-1), 38.1 (t, C-2), 34.4 (s, C-10), 31.9 (d, C-25), 30.0 (t, C-6), 28.5 (t, C-16), 25.4 (t, C-28), 23.0 (t ,C-15), 21.7 (t, C-11), 21.4 (q, C-21), 21.1 (q, C-27), 19.0 (q, C-26), 12.5 (q, C-19), 12.3 (q, C-29), 12.1 (q, C-18).

Simiarenol (2) – White powder; $[\alpha]_D^{25}$: +50.8° ($CHCl_3$, c = 0.3); EI-MS *m/z*: 426 [M^+]; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.62 (1H, dt, J = 2.0, 5.9 Hz, H-6), 3.47 (1H, br s, H-3), 1.14 (3H, s, Me-24), 1.05 (3H, s, Me-23), 1.00 (3H, s, Me-26), 0.92 (3H, s, Me-27), 0.89 (3H, s, Me-25), 0.88 (3H, d, J = 6.5 Hz, Me-29), 0.83 (3H, d, J = 6.5 Hz, Me-30), 0.78 (3H, s, Me-28). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 141.9 (s, C-5), 122.0 (d, C-6), 76.3 (d, C-3), 60.0 (d, C-21), 51.7 (d, C-18), 50.2 (d, C-10), 44.2 (d, C-8), 42.8 (s, C-17), 40.8 (s, C-4), 39.3 (s, C-14), 38.6 (s, C-13), 35.4 (t, C-16), 34.8 (s, C-9), 34.1 (t, C-11), 30.8 (d, C-22), 29.0 (t, C-15), 29.0 (q, C-23), 28.9 (t, C-12) , 28.3 (t, C-20), 27.7 (t, C-2), 25.5 (q, C-24), 24.0 (t, C-7), 22.9 (q, C-30), 21.9 (q, C-29), 19.9 (t, C-19), 18.0 (t, C-1), 17.8 (q, C-25), 16.1 (q, C-28), 15.7 (q, C-26), 15.0 (q, C-27).

Phytol (3) – Colorless oil; $[\alpha]_D^{25}$: +0.2° ($CHCl_3$, c = 0.3); EI-MS *m/z*: 296 [M^+]; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.30 (1H, td, J = 7.0, 1.2 Hz, H-2), 4.16 (2H, d, J = 6.8 Hz, H-1), 1.67 (3H, s, Me-3a), 0.86 (12H, d, J = 6.6 Hz, Me-7a, 11a, 15a, 16), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 140.3 (s, C-3), 123.0 (d, C-2), 59.4 (t, C-1), 39.9 (t, C-4), 39.3 (t, C-14), 37.4 (t, C-6), 37.3 (t, C-12), 37.3 (t, C-8), 36.6 (t, C-10), 32.8 (d, C-11), 32.7 (d, C-7), 28.0 (d, C-15), 25.1 (t, C-5), 24.8 (t, C-13), 24.5 (t, C-9), 22.7 (q, C-15a), 22.6 (q, C-16), 19.7 (q, C-11a), 19.7 (q, C-7a), 16.2 (q, C-3a).

Lupeol (4) – Colorless needles; $[\alpha]_D^{25}$: +28.1° ($CHCl_3$, c = 0.5); EI-MS *m/z*: 426 [M^+]; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.69 (1H, br d, J = 2.4 Hz, H-29b), 4.57 (1H, dd, J = 1.2, 2.4 Hz, H-29a), 3.19 (1H, dd, J = 5.1, 10.6 Hz, H-3), 2.38 (1H, m, H-19), 1.68 (3H, br s, Me-30), 1.03 (3H, s, Me-26), 0.97 (3H, s, Me-27), 0.94 (3H, s, Me-24), 0.83 (3H, s, Me-25), 0.79 (3H, s, Me-23), 0.76 (3H, s, Me-28); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.9 (s, C-20), 109.3 (t, C-29), 79.0 (d, C-3), 55.3 (d, C-5), 50.4 (d, C-9), 48.3 (d, C-19), 48.0 (d, C-18), 43.0 (s, C-17), 42.8 (s, C-14), 40.8 (s, C-8), 40.0 (t, C-22),38.8 (s, C-4), 38.7 (t, C-1), 38.0 (d, C-13), 37.1 (s, C-10), 35.6 (t, C-16), 34.2 (t, C-7), 29.8 (t, C-21), 28.0 (q, C-23), 27.4 (t, C-2), 27.3 (q, C-15), 25.1 (t, C-12), 20.9 (t, C-11), 19.3 (q, C-30), 18.3 (d, C-6), 18.0 (q, C-28), 16.1 (q, C-25), 15.9 (q, C-26), 15.4 (q, C-24), 14.5 (q, C-27).

α-Amyrin (5) – Colorless needles; $[\alpha]_D^{20}$: +83.5° ($CHCl_3$, c = 0.3); EI-MS *m/z*: 426 [M^+]; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.13 (1H, t, J = 4.0 Hz, H-12), 3.22 (1H, m, H-3), 1.07, 1.00, 0.99, 0.95, 0.79, 0.79 (each 3H, s, Me-27, 26, 23, 25, 24, 28), 0.91 (3H, d, J = 5.4 Hz, Me-30), 0.78 (3H, d, J = 5.4 Hz, Me-29); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.8 (s, C-13), 124.6 (d, C-29), 79.3 (d, C-3), 59.3 (d, C-18), 55.4 (d, C-5), 47.9 (d, C-9), 42.3 (s, C-14),

41.7 (t, C-22), 40.2 (s, C-8), 39.9 (d, C-19), 39.8 (d, C-20), 39.0 (t and s, C-1, 4), 37.1 (s, C-10), 38.0 (d, C-13), 34.0 (s, C-17), 33.1 (t, C-7), 31.5 (t, C-21), 29.0 (q, C-28), 28.3 (q, C-16), 28.3 (q, C-23), 27.5 (t, C-2), 26.8 (t, C-15), 23.6 (t, C-11), 23.5 (q, C-27), 21.6 (q, C-30), 18.6 (t, C-6),17.7 (q, C-29), 17.1 (q, C-26), 15.9 (q, C-24), 15.9 (q, C-24), 15.8 (q, C-25).

1β,4β-Dihydroxyeudesman-11-ene (6) – Colorless oil; $[\alpha]_D^{17}$: –29° ($CHCl_3$, $c = 0.05$); EI-MS *m/z*: 238 [M^+]; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.74 (1H, m, H-12a), 4.71 (1H, m, H-12b), 3.27 (1H, dd, $J = 4.8$, 11.4 Hz, H-1), 1.76 (3H, s, Me-13), 1.16 (3H, s, Me-15), 1.05 (3H, s, Me-14); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 150.5 (s, C-11), 108.6 (t, C-12), 79.7 (d, C-1), 71.4 (s, C-4), 50.4 (d, C-5), 46.1 (d, C-7), 39.4 (t, C-3), 39.3 (t, C-9), 38.9 (s, C-10), 30.0 (q, C-15), 26.8 (t, C-8), 26.4 (t, C-6), 25.6 (t, C-2), 20.8 (q, C-13), 12.6 (q, C-14).

3,7-Dihydroxyhumula-4,8(15),10(*E*)-triene (7) – Colorless oil; $[\alpha]_D^{20}$: +9.3° (MeOH, $c = 0.06$); EI-MS *m/z*: 236 [M^+]; ^{1}H NMR (600 MHz, CD_3OD) δ: 5.16 (1H, br s, H-15a), 4.99 (1H, br s, H-15b), 5.08 (1H, d, $J = 18$ Hz, H-11), 5.07 (1H, t, $J = 7.8$ Hz, H-5), 4.88 (1H, m, H-10), 4.07 (1H, dd, $J = 2.1$, 11.4, Hz, H-3), 3.87 (1H, dd, $J = 4.0$, 10.5 Hz, H-7), 1.57 (3H, br s, Me-14), 1.13 (3H, s, Me-12), 0.96 (3H, s, Me-13); ^{13}C NMR (150 MHz, CD_3OD) δ: 153.9 (s, C-8), 141.0 (s, C-4), 139.8 (d, C-11), 125.9 (d, C-5), 125.9 (d, C-10), 112.4 (t, C-15), 76.5 (d, C-3), 73.6 (d, C-7), 47.4 (t, C-2), 42.4 (t, C-9), 38.1 (t, C-6), 36.0 (s, C-1), 33.3 (q, C-13), 24.3 (q, C-14), 10.5 (q, C-12).

2,6-Dihydroxyhumula-3(12),7(13),9*E*-triene (8) – Colorless oil; $[\alpha]_D^{20}$: +4.3° (MeOH, $c = 0.05$); EI-MS *m/z*: 236 [M^+]; ^{1}H NMR (600 MHz, CD_3OD) δ: 5.41 (1H, d, $J = 15.9$ Hz, H-10), 5.34 (1H, m, H-9), 5.11 (1H, br s, H-12a), 4.86 (1H, br s, H-12b), 5.08 (1H, br s, H-13a), 4.94 (1H, br s, H-13b), 3.99 (1H, dd, $J = 5.2$, 8.3 Hz, H-6), 3.91 (1H, dd, $J = 2.0$, 6.3, Hz, H-2), 1.12 (3H, s, H-15), 1.00 (3H, s, H-14); ^{13}C NMR (150 MHz, CD_3OD) δ: 153.8 (s, C-3), 151.1 (s, C-7), 142.7 (d, C-10), 125.9 (d, C-9), 114.8 (t, C-13), 109.9 (t, C-12), 76.7 (d, C-6), 69.7 (d, C-2), 52.0 (t, C-1), 10.5 (q, C-12), 36.5 (s, C-11), 36.5 (t, C-8), 34.8 (t, C-5), 32.0 (t, C-4), 31.4 (q, C-14), 24.2 (q, C-15).

23-Hydroxybetulin (9) – Colorless needles; $[\alpha]_D^{20}$: +50.5° (MeOH, $c = 0.05$); EI-MS *m/z*: 426 [M^+]; ^{1}H NMR (500 MHz, CD_3OD) δ: 4.69 (1H, br s, H-29a), 4.57 (1H, br s, H-29b), 3.74 (1H, d, $J = 10.8$ Hz, H-28a), 3.28 (1H, d, $J = 10.8$ Hz, H-28b), 3.51 (1H, d, $J = 10.9$ Hz, H-23a), 3.28 (1H, d, $J = 10.9$ Hz, H-23b), 3.57 (1H, dd, $J = 5.1$, 10.6 Hz, H-3), 2.41 (1H, ddd, $J = 6.0$, 10.8, 10.8 Hz, H-19), 1.69 (3H, s, Me-30), 1.07 (3H, s, Me-26), 1.02 (3H, s, Me-27), 0.89 (3H, s, Me-25), 0.68 (3H, s, Me-24); ^{13}C NMR (125 MHz, CD_3OD) δ: 152.0 (s, C-20), 110.4 (t, C-29), 74.0 (d, C-3), 67.5 (t, C-23), 60.5 (t, C-28), 51.9 (d, C-9), 50.2 (d, C-18), 49.4 (d, C-19), 49.1 (d, C-5), 48.3 (d, C-19), 44.0 (s, C-14), 43.5 (s, C-4), 42.2 (s, C-8), 39.9 (t, C-1), 38.8 (d, C-13), 38.2 (s, C-10), 35.24 (t, C-16), 35.1 (t, C-7), 31.0 (t, C-21), 30.5 (t, C-15), 28.3 (t, C-16), 27.8 (t, C-2), 26.8 (t, C-12), 22.1 (t, C-11), 19.5 (d, C-30), 19.2 (t, C-6), 17.2 (q, C-25), 16.7 (q, C-26), 15.4 (q, C-27), 12.7 (q, C-24).

Results and Discussion

Repeated column chromatography of the CH_2Cl_2 soluble fraction of the aerial parts of *A. yomena* yielded nine terpenoids (**1 - 9)** (Fig. 1).

Compound **1** was obtained as white powder. It exhibited a mass peak at *m/z* 410 [M^+] corresponding to the molecular formula $C_{29}H_{46}O$ in the EI-MS spectrum. The ^{1}H NMR spectrum of **1** showed six methyl group protons at δ_H 1.04 (3H, d, $J = 6.7$ Hz, Me-21), 1.02 (3H, s, Me-19), 0.85 (3H, d, $J = 6.7$ Hz, Me-26), 0.81 (3H, t, $J = 7.3$ Hz, Me-29), 0.80 (3H, d, $J = 6.7$ Hz, Me-27) and 0.58 (3H, s, Me-18); three olefinic protons at δ_H 5.18 (1H, br s, H-7), 5.16 (1H, dd, $J = 8.5$, 15.2 Hz, H-22) and 5.03 (1H, dd, $J = 8.8$, 15.2 Hz, H-23). In the ^{13}C NMR spectrum, 29 carbon signals were observed, including one carbonyl carbon at δ_C 198.7, one olefinic quaternary carbon at δ_C 139.5, three olefinic methine carbons at δ_C 138.1, 129.5 and 117.0. From these results, compound **1** was indicated to be a steroid skeleton. Accordingly, compound **1** was determined as spinasterone on the basis of the above evidences, together with a comparison of the above data with those published in the literature (Akihisa *et al*., 1999; Ling *et al*., 2010).

Compound **2** was obtained as white powder. It exhibited a mass peak at *m/z* 426 [M^+] corresponding to the molecular formula $C_{30}H_{50}O$ in the EI-MS spectrum. The ^{1}H NMR spectrum of **2** showed eight methyl group protons at δ_H 1.14 (3H, s, Me-24), 1.05 (3H, s, Me-23), 1.00 (3H, s, Me-26), 0.92 (3H, s, Me-27), 0.89 (3H, s, Me-25), 0.88 (3H, d, $J = 6.5$ Hz, Me-29), 0.83 (3H, d, $J = 6.5$ Hz, Me-30) and 0.78 (3H, s, Me-28); one olefinic proton at δ_H 5.62 (1H, dt, $J = 2.0$, 5.9 Hz, H-6); one oxygenated methine proton at δ_H 3.47 (1H, br s, H-3). In the ^{13}C NMR spectrum, 30 carbon signals were observed, including one oxygenated carbon at δ_C 76.3, one olefinic quaternary carbon at δ_C 141.9, one olefinic methine carbon at δ_C 122.0. From these results, compound **2** was indicated to be a triterpenoid skeleton. Accordingly, compound **2** was determined as simiarenol on the basis of

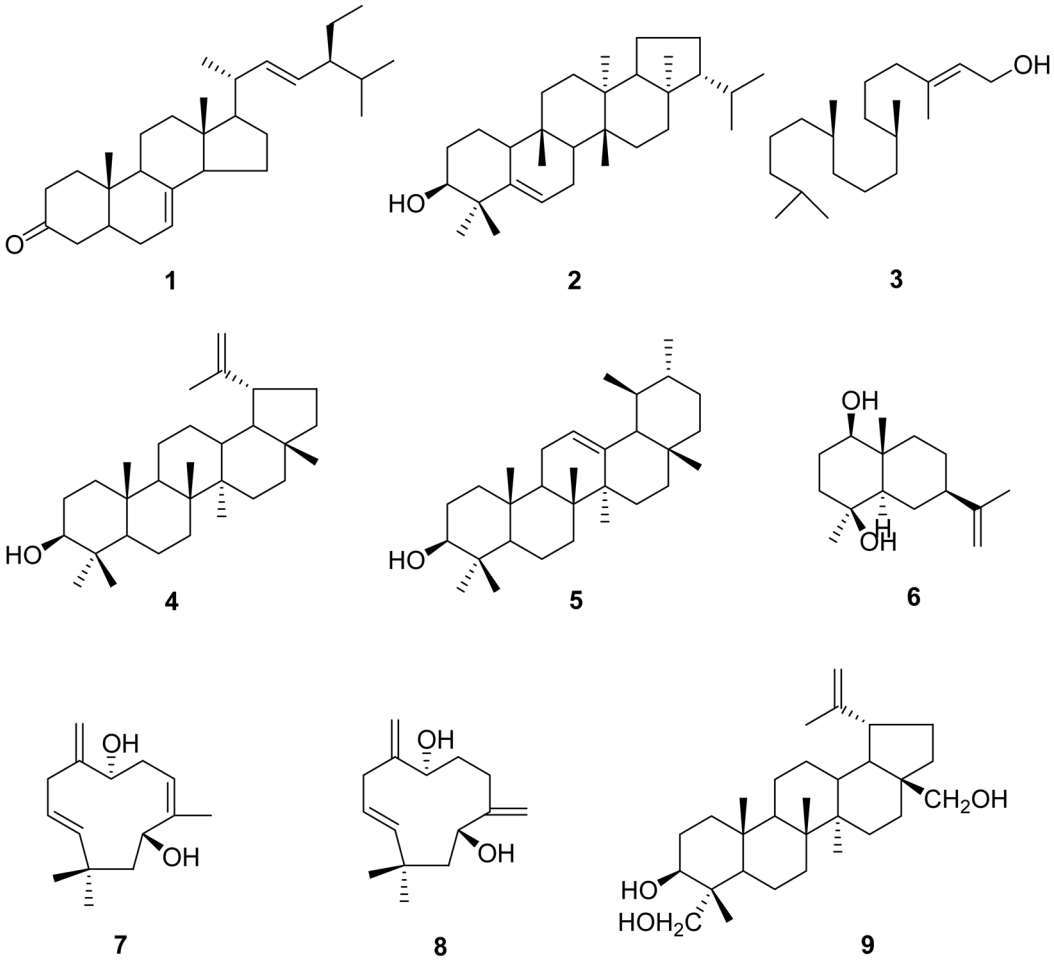

Fig. 1. Chemical structures of compounds **1 - 9**.

the above evidences, together with a comparison of the above data with those published in the literature (Tanaka *et al*., 1989).

Compound **3** was obtained as colorless oil. It exhibited a mass peak at *m/z* 296 $[M]^+$ corresponding to the molecular formula $C_{20}H_{40}O$ in the EI-MS spectrum. The ^1H NMR spectrum of **3** showed five methyl group protons at δ_H 1.67 (3H, s, Me-3a) and 0.86 (12H, d, J = 6.6 Hz, Me-7a, 11a, 15a, 16); one olefinic proton at δ_H 5.30 (1H, td, J = 1.2, 7.0 Hz, H-2); one oxygenated methylene proton at δ_H 4.16 (2H, d, J = 6.8 Hz, H-1). In the ^{13}C NMR spectrum, 20 carbon signals were observed, including one oxygenated carbon at δ_C 59.4, one olefinic quaternary carbon at δ_C 140.3, one olefinic methine carbon at δ_C 123.0. From these results, compound **3** was indicated to be a diterpene skeleton. Accordingly, compound **3** was determined as phytol on the basis of the above evidences, together with a comparison of the above data with those published in the literature (Brownstein *et al*., 1989).

Compound **4** was obtained as colorless needles. It exhibited a mass peak at *m/z* 426 $[M]^+$ corresponding to the molecular formula $C_{30}H_{50}O$ in the EI-MS spectrum. The ^1H NMR spectrum of **4** showed seven methyl group protons at δ_H 1.68 (3H, br s, Me-30), 1.03 (3H, s, Me-26), 0.97 (3H, s, Me-27), 0.94 (3H, s, Me-24), 0.83 (3H, s, Me-25), 0.79 (3H, s, Me-23) and 0.76 (3H, s, Me-28); two vinylic protons of terminal methylene group at δ_H 4.69 (1H, br d, J = 2.4 Hz, H-29b) and 4.57 (1H, dd, J = 1.2, 2.4 Hz, H-29a); one oxygenated methine proton at δ_H 3.19 (1H, dd, J = 5.1, 10.6 Hz, H-3). In the ^{13}C NMR spectrum, 30 carbon signals were observed, including one exo-methylene carbon at δ_C 109.3; one oxygenated carbon at δ_C 79.0. From these results, compound **4** was indicated to be a lupane type triterpenoid. Accordingly, compound **4** was determined as lupeol on the basis of the above evidences, together with a comparison of the above data with those published in the literature (Jung *et al*., 2008 and Fotie *et al*., 2006).

Compound **5** was obtained as colorless needles. It exhibited a mass peak at *m/z* 426 $[M]^+$ corresponding to the molecular formula $C_{30}H_{50}O$ in the EI-MS spectrum. The ^1H NMR spectrum of **5** showed six methyl group protons at δ_H 1.07, 1.00, 0.99, 0.95, 0.79 and 0.79 (each 3H, s, Me-27, 26, 23, 25, 24, 28); two secondary methyl protons at δ_H 0.91 (3H, d, J = 5.4 Hz, Me-30) and 0.78 (3H, d, J = 5.4 Hz, Me-29); one oxygenated methine proton at δ_H 3.22 (1H, m, H-3). In the ^{13}C NMR spectrum, 30 carbon signals were observed, including one oxygenated carbon at δ_C 79.3, one olefinic quaternary carbon at δ_C 139.8, one olefinic methine carbon at δ_C 124.6. From these results, compound **5** was indicated to be an ursane type triterpenoid. Accordingly, compound **5** was determined as α-amyrin on the basis of the above evidences, together with a comparison of the above data with those published in the literature. (Lee *et al*., 2003)

Compound **6** was obtained as colorless oil. It exhibited a mass peak at *m/z* 296 $[M]^+$ corresponding to the molecular formula $C_{20}H_{40}O$ in the EI-MS spectrum. The ^1H NMR spectrum of **6** showed three methyl group protons at δ_H 1.76 (3H, s, Me-13), 1.16 (3H, s, Me-15) and 1.05 (3H, s, Me-14); two vinylic protons of terminal methylene group at δ_H 4.74 (1H, m, H-12a) and 4.71 (1H, m, H-12b); one oxygenated methine proton at δ_H 3.27 (1H, dd, J = 4.8, 11.4 Hz, H-1). In the ^{13}C NMR spectrum, 15 carbon signals were observed, including two oxygenated carbon at δ_C 79.7 and 71.4; one exo-methylene carbon at δ_C 108.6. From these results, compound **6** was indicated to be an eudesmane type sesquiterpenoid. Accordingly, compound **6** was determined as 1β,4β-dihydroxyeudesman-11-ene on the basis of the above evidences, together with a comparison of the above data with those published in the literature. (Li *et al*., 2005)

Compound **7** was obtained as colorless oil. It exhibited a mass peak at *m/z* 236 $[M]^+$ corresponding to the molecular formula $C_{15}H_{24}O_2$ in the EI-MS spectrum. The ^1H NMR spectrum of **7** showed three methyl group protons at δ_H 1.57 (3H, br s, Me-14), 1.13 (3H, s, Me-12) and 0.96 (3H, s, Me-13); two vinylic protons of terminal methylene group at δ_H 5.16 (1H, br s, H-15a) and 4.99 (1H, br s, H-15b); three olefinic protons at δ_H 5.08 (1H, d, J = 18.0 Hz, H-11), 4.88 (1H, m, H-10) and 5.07 (1H, t, J = 7.8 Hz, H-5); two oxygenated methine protons at δ_H 4.07 (1H, dd, J = 2.1, 11.4 Hz, H-3) and 3.87 (1H, dd, J = 4.0, 10.5 Hz, H-7). In the ^{13}C NMR spectrum, 15 carbon signals were observed, including two oxygenated carbons at δ_C 76.5 and 73.6; one exo-methylene carbon at δ_C 112.4; one olefinic quaternary carbon at δ_C 141.0; three olefinic methine carbons at δ_C 139.8, 125.9 and 125.9. From these results, compound **7** was indicated to be a humulane type sesquiterpenoid. Accordingly, compound **7** was determined as 3,7-dihydroxyhumula-4,8(15),10(*E*)-triene on the basis of the above evidences, together with a comparison of the above data with those published in the literature (Smith *et al*., 1991; Xu *et al*., 2004).

Compound **8** was obtained as colorless oil. It exhibited a mass peak at *m/z* 236 $[M]^+$ corresponding to the molecular formula $C_{15}H_{24}O_2$ in the EI-MS spectrum. Its ^1H, ^{13}C NMR spectra was quite similar to those of compound **7**. But, the ^1H-NMR spectrum of **8** showed two methyl group protons at δ_H 1.12 (3H, s, Me-15) and 1.00 (3H, s, Me-14); two vinylic protons of terminal methylene group at δ_H 5.11 (1H, br s, H-12a) and 4.86 (1H, br s, H-12b), two more vinylic protons of terminal methylene group at δ_H 5.08 (1H, br s, H-13a) and 4.94 (1H, br s, H-13b); two olefinic protons at δ_H δ5.41 (1H, d, J = 15.9 Hz, H-10) and 5.34 (1H, m, H-9); another two oxygenated methine protons at δ_H 3.91 (1H, dd, J = 2.0, 6.3 Hz, H-2) and 3.99 (1H, dd, J = 5.2, 8.3, H-6). In the ^{13}C NMR spectrum, 15 carbon signals were observed, including two oxygenated carbons at δ_C 69.7 and 76.7; two exo-methylene carbons at δ_C 109.9 and 114.8; two olefinic methine carbons at δ_C 142.7 and 125.9. From these results, compound **8** was indicated to be a humulane type sesquiterpenoid. Accordingly, compound **8** was determined as 2,6-dihydroxyhumula-3(12),7(13),9*E*-triene on the basis of the above evidences, together with a comparison of the above data with those published in the literature. (Li *et al*., 2007)

Compound **9** was obtained as colorless needles. It exhibited a mass peak at *m/z* 458 $[M]^+$ corresponding to the molecular formula $C_{30}H_{50}O_3$ in the EI-MS spectrum. Its NMR spectrum pattern was quite similar to those of compound **4**. The ^1H NMR spectrum of **9** showed five methyl group protons at δ_H 1.69 (3H, s, Me-30), 1.07 (3H, s, Me-26), 1.02 (3H, s, Me-27), 0.89 (3H, s, Me-25) and 0.68 (3H, s, Me-24); two vinylic protons of terminal methylene group at δ_H 4.69 (1H, br s, H-29a) and 4.57 (1H, br s, H-29b); two oxygenated methylene protons at δ_H 3.74 (1H, d, J = 10.8 Hz, H-28a), 3.28 (1H, d, J = 10.8 Hz, H-28b), 3.51 (1H, d, J = 10.9 Hz, H-23a) and 3.28 (1H, d, J = 10.9 Hz, H-23b); one oxygenated methine proton at δ_H 3.57 (1H, dd, J = 5.1, 10.6 Hz, H-3). In the ^{13}C NMR spectrum, 30 carbon signals were observed, including one exo-methylene carbon at δ_C 110.4; three oxygenated carbons at δ_C 74.0, 67.5 and 60.5. From these results, compound **9** was indicated to be a lupane type triterpenoid. Accordingly, compound **9** was determined as 23-hydroxybetulin on the basis of the above evidences,

together with a comparison of the above data with those published in the literature (Guerrero-Analco *et al*., 2010).

In this study, nine terpenoids were isolated from *A. yomena*. To the best of our knowledge, these compounds were isolated from this plant for the first time.

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