SUPPLEMENTARY MATERIAL

Chemical constituents from *Agrimonia pilosa* Ledeb. and their chemotaxonomic significance

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Abstract

Phytochemical investigation of the ethanol extract from the whole plant of *Agrimonia pilosa* led to the isolation of thirty one compounds, including sixteen flavonoids (**1**-**16**), five triterpenes (**17**-**21**), one isocoumarin (**22**), five phenolic acids (**23**-**27**), one ceramide (**28**), two agrimols (**29**-**30**) and one fatty acid (**31**). Their structures were determined by various spectroscopic analysis. Compounds **5**, **7** and **20** were firstly isolated from the genus Agrimonia, and compounds **6**, **10**-**11**, **15**, **26**, **28** and **31** were isolated from the family Rosaceae for the first time. Moreover, the chemotaxonomic significance of these compounds was summarized.

Key words: *Agrimonia pilosa* Ledeb., Flavonoids, Triterpenoids, Phenolic derivatives, Chemotaxonomy

1. Experimental

1.1 General

IR spectra were recorded on a Bruker Tensor 27 spectrometer with KBr-disks (Bruker, Karlsruhe, Germany). Mass spectra were obtained on a MS Agilent 1100 Series LC/MSD Trap mass spectrometer (ESI-MS). NMR spectra were measured on a Bruker AV-300 NMR and a Bruker AV-500 NMR spectrometers with TMS as an internal standard. HR-ESI-MS spectra was conducted on a Mariner API-TOF mass spectrometer. Column chromatography was done with silica gel (Qingdao marine Chemical Co., Ltd., P.R.China) , ODS (40-63 μm, Fuji, Japan) and Sephedex LH-20 (Uppsala, Sweden). TLC analysis was carried out on precoated silica gel GF254 plates(Qingdao marine Chemical Co., Ltd., P.R.China) and RP_{18}(200μm, Merck, Darmstadt, Germany). All chemical solvents used in this study were of analytical grade.

1.2 Plant material

The *Agrimonia pilosa* sample was collected from Jiangsu Province, China and identified by Prof. She-Ban Pu (China Pharmaceutical University, Nanjing 210009, China). A voucher specimen (20130512) was deposited at Department of Natural Medicinal Chemistry, China Pharmaceutical University, Nanjing 210009, China.

1.3 Extraction and isolation

The whole plants of *Agrimonia pilosa* (9 kg) were extracted with 80% EtOH four times. The extract solutions were combined and concentrated by rotary evaporator at 60 ℃. The residue (1500 g) was suspended in H_2O and extracted with petroleum ether (PE), EtOAc and n-butanol. The EtOAc fraction (86 g) was subjected to column chromatography (CC) over silica gel (200-300 mesh) using a CH_2Cl_2-MeOH gradient (50:1, 30:1, 20:1, 10:1, 5:1, 3:1, v/v) to afford six fractions (fraction A-F). Fraction B was subjected to a macroporous resin D101 column eluted by water-MeOH (70:30, 50:50, 30:70, v/v) to yield three fractions (subfraction B1-B3). Subfraction B2 (1 g) was chromatographed on an ODS column eluted by water-MeOH (100:0, 70:30, 60:40, 50:50, 40:60, 30:70, 0:100, v/v), and then isolated by silica gel CC (200-300 mesh, eluted by CH_2Cl_2/MeOH), after purified by Sephadex LH-20 with MeOH, compounds **2** (50 mg), **3** (17 mg), **4** (25 mg) and **23** (10 mg) were afforded. Subfraction B1 (2 g) was repeatedly isolated by silica gel CC with CH_2Cl_2/MeOH as elution solvent and further purified by Sephadex LH-20 with CH_2Cl_2/MeOH (1:1, v/v) to afford compounds **15** (10 mg), **24** (50 mg), **25** (7 mg), **26** (20 mg) and **27** (30 mg). Subfraction B3 (2 g) was subjected to silica gel CC eluted by CH_2Cl_2/EtOAc, then chromatographed on an ODS column eluted by water-MeOH to afford compound **17** (5 mg). Fraction A was subjected to silica gel CC eluted by PE/EtOAc and further isolated by ODS coloumn, finally purified by recrystal to yield compounds **18** (10 mg), **19** (340 mg), **20** (300 mg), and **21** (20 mg). Fraction C (9 g) was isolated by silica gel CC, futher seperated by ODS column eluted by water-MeOH (40:60, 30:70, 20:80, v/v), and then purified by Sephadex LH-20 with MeOH to afford compounds **5** (4 mg), **6** (5 mg), **7** (3 mg), **8** (5 mg), **9** (20 mg), **10** (5 mg), **11** (11 mg), **13** (4 mg), **16** (10 mg), and **22** (70 mg). Fraction D (18 g) was repeatedly seperated by silica gel CC eluted by CH_2Cl_2/MeOH to afford compounds **1** (400 mg), **12** (170 mg), **28** (10 mg), and **31** (8 mg). Fraction E was chromatographed on an ODS column, eluted by water-MeOH (40:60,

30:70, 20:80, v/v) and then purified by sephadex LH-20 with MeOH to afford compound **14** (10 mg).

The dried PE residue was subjected to silica gel CC eluted by PE/EtOAc (50:1, 30:1, 10:1, 5:1, 3:1, v/v) to afford five fractions (Fraction A-E). Fraction B was repeatedly isolated by silica gel CC eluted by PE/EtOAc to afford two agrimols, compounds **29** (50 mg), and **30** (20 mg).

1.4 Spectral and experimental data of the isolated compounds

Compound **1**: Yellow powder (MeOH); mp:135~140℃; ESI-MS m/z:595.13 $[M+H]^+$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 12.59 (1H, s, 5-OH), 10.82 (1H, s, 7-OH), 10.13 (1H, s, 4'-OH), 9.99 (1H, s, 4'''-OH), 6.18 (1H, s, 6-H), 6.41 (1H, s, 8-H), 8.02 (2H, brs, 2', 6'-H), 6.89 (2H, brs, 3', 5'-H), 7.38 (2H, brs), 6.82 (2H, brs), 6.14 (1H, d, *J* = 15.0 Hz), 7.37 (1H, d, *J* = 15.0 Hz), 5.47 (1H, brs, 1''-H), 4.31 (1H, d, *J* = 10.6 Hz, 6''-H), 4.07 (1H, brs, 6''-H), 3.2~3.4 (4H, m, Glc-H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C 156.4 (C-2), 133.1 (C-3), 177.4 (C-4), 161.1 (C-5), 98.9 (C-6), 164.1 (C-7), 93.8 (C-8), 156.3 (C-9), 103.9 (C-10), 124.9 (C-1'), 130.1 (C-2',6'), 115.7 (C-3', 5'), 159.8 (C-4'), 101.0 (C-1''), 74.2 (C-2''), 76.2 (C-3''), 70.0 (C-4''), 74.1 (C-5''), 63.0 (C-6''), 113.6 (C-α), 144.6 (C-β), 124.9 (C-1'''), 130.1 (C-2''', 6'''), 115.7 (C-3''', 5'''), 159.8 (C-4''').

Compound **2**: Yellow powder (MeOH); mp:313~314℃; ESI-MS m/z:300.96 $[M-H]^-$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 12.47 (1H, s, 5-OH), 10.72 (1H, s, 3-OH), 9.52 (1H, s, -OH), 9.28 (1H, s, -OH), 9.24 (1H, s, -OH), 7.68(1H, d, *J* = 1.9 Hz, 2'-H), 7.54 (1H, dd, *J* = 8.4, 1.9 Hz, 6'-H), 6.89 (1H, d, *J* = 8.4 Hz, 5'-H), 6.40 (1H, d, *J* = 1.8 Hz, 8-H), 6.19 (1H, d, *J* = 1.8 Hz, 6-H).

Compound **3**: Yellow powder (MeOH); mp:328~330℃; ESI-MS m/z:287.06 $[M+H]^+$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 12.96 (1H, s, 5-OH), 10.77 (1H, s, 7-OH), 9.85 (1H, s, 4'-OH), 9.34 (1H, s, 3'-OH), 7.42 (1H, brs, 6′-H), 7.40 (1H, s, 2′-H), 6.89 (1H, d, *J* = 8.15 Hz, 5′-H), 6.65 (1H, s, 3-H), 6.44 (1H, s, 8-H), 6.20 (1H, s, 6-H).

Compound **4**: Yellow powder (MeOH); mp:328~330℃; ESI-MS m/z:287.06 $[M+H]^+$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 12.96 (1H, s, 5-OH), 10.77 (1H, s, 7-OH), 9.85 (1H, s, 4'-OH), 9.34 (1H, s, 3'-OH), 7.42 (1H, brs, 6′-H), 7.40 (1H, s, 2′-H), 6.89 (1H, d, *J* = 8.15 Hz, 5′-H), 6.65 (1H, s, 3-H), 6.44 (1H, s, 8-H), 6.20 (1H, s, 6-H).

Compound **5**: White crystals (MeOH); mp:130~132℃; ESI-MS m/z:419.11 $[M+H]^+$; ^{1}H-NMR (500 MHz, DMSO-d6) δ_H 12.01 (1H, s, 5-OH), 5.65 (1H, dd, *J* = 12.6, 2.5 Hz, 2-H), 3.23 (1H, m, 3a-H), 2.86 (1H, dd, *J* = 17.1, 2.5 Hz, 3b-H), 7.53 (2H,d, *J* = 7.5 Hz, 2', 6'-H), 7.43(3H, m, 3', 4', 5'-H), 6.20 (1H, s, 8-H), 6.16 (1H, s, 6-H), 4.97 (1H, d, *J* = 7.4, 1''-H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C 78.6 (C-2), 42.2 (C-3), 196.7 (C-4), 162.9 (C-5, 9), 96.6 (C-6), 165.3 (C-7), 95.5 (C-8), 103.3 (C-10), 138.4 (C-1'), 126.7 (C-2', 6'), 128.6 (C-3', 5'), 128.5 (C-4'), 99.6 (C-1''), 73.0 (C-2''), 76.3 (C-3''), 69.5 (C-4''), 77.1 (C-5''), 60.6 (C-6'').

Compound **6**: White granular crystal (MeOH); ESI-MS m/z:397.14 $[M+H]^+$, ^{1}H-NMR (500 MHz, CD_3OD)中 δ_H 6.69 (1H, d, *J* = 1.9 Hz, 8-H), 6.48 (1H, d, *J* = 1.9 Hz, 6-H), δ_H 6.11 (1H, s, 3-H), δ_H 0.95 (3H, t, *J* = 7.4 Hz, 3′-H), 1.30 (3H, d, *J* = 7.0 Hz, 4′-H), δ_H 2.67 (1H, tq, *J* = 7.0, 7.0 Hz, 1′-H), δ_H 1.76 (1H, dq, *J* = 7.0, 7.0 Hz, 2′a-H), δ_H 1.64 (1H, dq, *J* = 7.0, 7.0 Hz, 2′b-H), δ_H 5.04 (1H, d, *J* = 7.1 Hz), δ_H 3.91 (1H, brd, *J* = 12.0 Hz), 3.70 (1H, dd, *J* = 12.0, 5.7 Hz); ^{13}C-NMR (125 MHz, CD_3OD) δ_C 184.3, 41.8 (C-1′), 28.6 (C-2′), 18.2 (C-4′), 11.9 (C-3′), 176.5 (C-2), 164.8

(C-7), 163.0 (C-5), 159.5 (C-9), δ_C 107.1 (C-10), 108.0 (C-3), 101.1 (C-6), 96.0 (C-8), δ_C 101.7 (C-1″), 74.7 (C-2″), 77.9 (C-3″), 71.3(C-4″), 78.4 (C-5″), 62.4 (C-6″)。

Compound **7**: Yellow powder (MeOH); ESI-MS m/z:419.06 $[M+H]^+$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 12.67 (1H, s, 5-OH), 10.87 (1H, s, 7-OH), 10.19 (1H, s, 4′-OH). δ_H 6.49 (1H, d, J = 1.9 Hz, 8-H), 6.26 (1H, d, J = 1.9 Hz, 6-H), 8.07 (2H, d, J = 8.8 Hz, 2′, 6′-H), 6.95 (2H, d, J = 8.8 Hz, 3′, 5′-H), 5.68 (1H, s, 1″-H), 3.3~4.2 (8H, m, Ala-H).

Compound **8**: Yellow powder (MeOH); mp:276~278℃; ESI-MS m/z:419.06 $[M+H]^+$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 12.47 (1H, s, 5-OH), 10.75 (1H, s, 7-OH), 10.07 (1H, s, 4′-OH), 9.35 (1H, s, 3-OH). δ_H 8.04 (2H, d, J = 8.7 Hz, 2′, 6′-H), 6.92 (2H, d, J = 8.7 Hz, 3′, 5′-H), 6.43 (1H, d, J = 1.8 Hz, 8-H), 6.19 (1H, d, J = 1.8 Hz, 6-H).

Compound **9**: White cluster crystal (MeOH); mp 175~177 ℃; ESI-MS m/z:291.04 $[M+H]^+$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 9.11 (1H, s, -OH), 8.89 (1H, s, -OH), 8.80 (1H, s, -OH), 8.75 (1H, s, -OH), 2.66 (1H, dd, J = 16.0, 5.2 Hz, 4β-H), 2.36 (1H, dd, J = 16.0, 8.0 Hz, 4α-H), 3.82 (1H, m, 3-H), 4.48 (1H, d, J = 7.4 Hz, 2-H), 5.69 (1H, s, 6-H), 5.89 (1H, s, 8-H), 6.59 (1H, d, J = 8.0 Hz, 6′-H), 6.69 (1H, d, J = 8.0 Hz, 5′-H), 6.72 (1H, s, 2′-H).

Compound **10**: Light yellow grains (MeOH); ESI-MS m/z 491.11 $[M+H]^+$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 12.56 (1H, s, 5-OH), 10.85 (1H, s, 7-OH), 10.15 (1H, s, 4′-OH), 6.24 (1H, brs, 6-H), 6.47 (1H, brs, 8-H), 8.02 (2H, d, J = 7.6 Hz, 2′, 6′-H), 6.90 (2H, d, J = 7.5 Hz, 3′, 5′-H), 5.15 (1H, d, J = 7.3 Hz, 1″-H), 5.37 (1H, brs, Glc-OH), 5.39 (1H, d, J = 3.7 Hz, Glc-OH), 5.11 (1H, d, J = 3.7 Hz, Glc-OH), 4.14 (1H, d, J = 11.5 Hz, 6″a-H), 3.98 (1H, d, J = 11.6, 5.4 Hz, 6″b-H), 3.16~3.35 (4H, m, Glc-H), 1.77 (3H, s, -CH_3); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C 170.1 (-$COCH_3$), 20.3 (-CH_3), 156.6 (C-2), 133.2 (C-3), 177.6 (C-4), 161.4 (C-5), 98.9 (C-6), 164.4 (C-7), 93.9 (C-8), 156.8 (C-9), 104.1 (C-10), 121.0 (C-1′), 131.0 (C-2′, 6′), 115.3 (C-3′, 5′), 160.2 (C-4′), 101.3 (C-1″), 74.1 (C-2″), 74.3 (C-3″), 70.0 (C-4″), 76.3 (C-5″), 62.9 (C-6″).

Compound **11**: Pink powder (Acetone); ESI-MS m/z:435.04 $[M-H]^-$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 9.66 (1H, s, -OH), 9.25 (1H, s, -OH), 8.85 (2H, s, -OH), 4.59 (1H, d, J = 7.4 Hz, 2-H), 3.94 (1H, m, 3-H), 2.59 (1H, d, J = 7.4 Hz, 4-H), 2.83 (1H, m, 4-H), 6.17 (1H, s, 8-H), 6.74 (1H, brs, 2′-H), 6.70 (1H, brs, 5′-H), 6.68 (1H, brs, 6′-H), 6.89 (2H, d, J = 8.2 Hz, 2″, 6″-H), 6.64 (2H, brs, 3″, 5″-H), 3.11 (1H, m, α–H), 2.78 (1H, m, α–H), 4.38 (1H, d, J = 6.3 Hz, β–H); ^{13}C-NMR (75 MHz, DMSO-d_6) δ_C 81.3 (C-2), 65.6 (C-3), 27.3 (C-4), 150.1 (C-5), 105.4 (C-6), 154.0 (C-7), 98.3 (C-8), 153.1 (C-9), 100.1 (C-10), 130.1 (C-1′), 114.5 (C-2′), 144.9 (C-3′), 145.0 (C-4′), 115.2 (C-5′), 118.4 (C-6′), 132.2 (C-1″), 127.6 (C-2″, 6″), 115.3 (C-3″, 5″), 156.1 (C-4″), 167.8 (-COO-), 37.0 (C-α), 33.1 (C-β).

Compound **14**: Yellow powder (MeOH-$CHCl_3$); mp:206~208℃; ESI-MS m/z:463.08 $[M-H]^-$; ^{1}H-NMR (300 MHz, DMSO-d_6) δ_H 12.61 (1H, s, 5-OH), 10.80 (1H, s, 7-OH), 9.24 (2H, s, 3′,4′-OH), 6.38 (1H, brs, 8-H), 6.18 (1H, brs, 6-H), 6.82 (1H, d, J = 8.9 Hz, 5′-H), 7.55 (2H, brs, 2′, 6′-H), Glc-H:5.44 (1H, d, J = 6.7 Hz, 1″-H), 5.24 (1H, s), 5.01 (1H, s), 4.91 (1H, s), 4.21 (1H, s), 3.56 (2H, d, J = 11.4 Hz), 3.20 (2H, brs), 3.06 (2H, brs).

Compound **15**: White granular crystal (MeOH); mp:240~241℃; ESI-MS m/z:288.86 $[M+H]^+$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 11.89 (1H, s, 5-OH), 10.78 (1H, s, 7-OH), 9.51 (1H, s, 4′-OH), 7.31 (2H, d, J = 8.4 Hz, 2′ ,6′-H), 6.78 (2H, d, J = 8.4 Hz, 3′, 5′-H), 5.91 (1H, d, J = 1.6 Hz, 8-H),

5.86 (1H, d, *J* = 1.6 Hz, 6-H), 5.72 (1H, d, *J* = 6.2 Hz, 3-OH), 5.05 (1H, d, *J* = 11.4 Hz, 2-H), 4.57 (1H, dd, *J* = 11.4, 6.2 Hz, 3-H). .

Compound **16**: White powder (MeOH); mp:230~233℃; ESI-MS m/z:302.87 $[M-H]^-$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 11.91 (1H, s, 5-OH), 10.91 (1H, s, 7-OH), 9.01 (1H, s, -OH), 8.96 (1H, s, -OH), 6.89 (1H, brs, 2′-H), 6.76(2H, brs, 5′, 6′-H), 5.93 (1H, d, *J* = 1.7 Hz, 8-H), 5.89 (1H, d, *J* = 1.7 Hz, 6-H), 5.75 (1H, d, *J* = 5.9 Hz, 3-OH), 5.01 (1H, d, *J* = 11.1 Hz, 2-H), 4.51 (1H, dd, *J* = 11.1, 6.1 Hz, 3-H).

Compound **17**: White powder (MeOH-$CHCl_3$); mp:260~262℃; ESI-MS m/z:506.35 $[M+NH_4]^+$, 523.42 $[M+Cl]^-$; ^{1}H-NMR (500 MHz, C_5D_5N) δ_H 1.05 (3H, s, 25-H), 1.10 (3H, s, 24-H), 1.13 (6H, brs, 26, 30-H), 1.29 (3H, s, 23-H), 1.46 (3H, s, 29-H), 1.73 (3H, s, 27-H), 5.59 (1H, s, 12-H), 4.11(1H, m, 2α-H), 3.4(1H, d, *J* = 9.3 Hz, 3β-H), 3.07(1H, s, 18-H); ^{13}C-NMR (125 MHz, C_5D_5N) δ_C 48.3 (C-1), 69.0 (C-2), 84.2 (C-3), 40.2 (C-4), 56.3 (C-5), 19.4 (C-6), 33.9 (C-7), 40.8 (C-8), 48.2 (C-9), 38.9 (C-10), 24.5 (C-11), 128.3 (C-12), 140.1 (C-13), 42.5 (C-14), 29.7 (C-15), 26.8 (C-16), 48.7 (C-17), 55.0 (C-18), 73.1 (C-19), 42.7 (C-20), 27.5 (C-21), 38.9 (C-22), 29.6 (C-23), 18.0 (C-24), 17.1 (C-25), 17.6 (C-26), 25.1 (C-27), 181.0 (C-28), 27.3 (C-29), 17.2 (C-30).

Compound **18**: White powder (MeOH-$CHCl_3$); mp:293~295℃。ESI-MS m/z:507.34 $[M+Cl]^-$, ^{1}H-NMR (300 MHz, C_5D_5N) δ_H 5.63 (1H, brs, 12-H), 3.46 (1H, m, 3-H), 3.08 (1H, s, 18-H), 1.75 (3H, s, -CH_3), 1.47 (3H, s, -CH_3), 1.26 (3H, s, -CH_3), 1.15 (3H, s, -CH_3), 1.14 (3H, brs, -CH_3), 1.05 (3H, s, -CH_3), 0.95 (3H, s, -CH_3); ^{13}C-NMR (75 MHz, C_5D_5N) δ_C 39.4 (C-1), 28.5 (C-2), 78.6 (C-3), 39.8 (C-4), 56.3 (C-5), 19.4 (C-6), 34.0 (C-7), 40.8 (C-8), 48.7 (C-9), 37.8 (C-10), 24.4 (C-11), 128.5 (C-12), 140.3 (C-13), 42.5 (C-14), 29.7 (C-15), 26.8 (C-16), 48.2 (C-17), 55.0 (C-18), 73.1 (C-19), 42.8 (C-20), 27.5 (C-21), 38.9 (C-22), 29.2 (C-23), 16.0 (C-24), 16.9 (C-25), 17.6 (C-26), 25.1 (C-27), 181.0 (C-28), 27.3 (C-29), 17.1 (C-30).

Compound **19**: White powder (MeOH-$CHCl_3$); ESI-MS m/z:537.32 $[M+Cl]^-$, 520.19 $[M+NH_4]^+$; ^{1}H-NMR (300 MHz, C_5D_5N) δ_H 1.81 (3H, s, 27-H), 1.44 (3H, s, 29-H), 1.36 (3H, s, 23-H), 1.15 (3H, s, 26-H), 1.14 (3H, d, *J* = 8.4 Hz, 30-H), 0.97 (3H, s, 25-H), 0.91 (3H, s, 24-H), δ_H 5.72 (1H, s), δ_H 4.37 (1H, s, 1-H), 4.33 (1H, s, 3-H), 3.14 (1H, m, 16-Ha), 3.08 (1H, s, 18-H); ^{13}C-NMR (75 MHz, C_5D_5N) δ_C 212.5 (C-2), 181.0 (C-28), 129.4 (C-12), 139.3 (C-13), 85.6 (C-1), 82.2 (C-3), 73.1 (C-19), 29.7 (C-23), 17.5 (C-24), 12.8 (C-25), 17.4 (C-26), 25.0 (C-27), 27.5 (C-29), 17.1 (C-30).

Compound **20**: White powder (MeOH-$CHCl_3$); mp:253~255℃; ESI-MS m/z:507.36 $[M+Cl]^-$, 490.37 $[M+NH_4]^+$; ^{1}H-NMR (500 MHz, C_5D_5N) δ_H 1.29 (3H, s, -CH_3), 1.23 (3H, s, -CH_3), 1.09 (3H, s, -CH_3), 1.07 (3H, s, -CH_3), 1.02 (3H, d, *J* = 6.8Hz, 30-H), 1.01 (3H, s, -CH_3), 0.98 (3H, d, *J* = 6.8Hz, 29-H), 5.48 (1H, s, 12-H), 4.08 (1H, m, 2-H), 3.40 (1H, d, *J* = 9.3 Hz, 3-H); ^{13}C-NMR (125MHz, C_5D_5N) δ_C 48.4 (C-1), 69.0 (C-2), 84.2 (C-3), 40.4 (C-4), 56.3 (C-5), 19.2 (C-6), 33.9 (C-7), 40.2 (C-8), 48.5 (C-9), 38.8 (C-10), 24.1 (C-11), 125.9 (C-12), 139.7(C-13), 42.9 (C-14), 29.0 (C-15), 25.3 (C-16), 48.5 (C-17), 53.9 (C-18), 39.8 (C-19), 39.9 (C-20), 31.4 (C-21), 37.8 (C-22), 29.7 (C-23), 18.1 (C-24), 17.3 (C-25), 17.9 (C-26), 24.3 (C-27), 180.2 (C-28), 17.8 (C-29), 21.8 (C-30).

Compound **22**: White powder (MeOH-$CHCl_3$); mp:165~167℃; ESI-MS:m/z 477.15 $[M+H]^+$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 11.14 (1H, s, 8-OH), 7.21 (2H, d, *J* = 8.1 Hz, 2', 6'-H), 6.90

(2H, d, *J* = 8.1 Hz, 3', 5'-H), 6.54 (2H, s, 5, 7-H), 2.00 (1H, m, 1"-H), 2.07 (1H, m, 1"-H), 2.79 (1H, m, 2"-H), 2.70 (1H, m, 2"-H), 3.02 (2H, m, 4-H), 3.76 (3H, s, 4'-OCH_3), 4.59 (1H, m, 3-H), 5.01 (1H, d, *J* = 7.4 Hz, Glc-1-H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ_C 169.1 (C-1), 78.3 (C-3), 32.1 (C-4), 107.2 (C-5), 163.0 (C-6), 102.4 (C-7), 163.0 (C-8), 101.7 (C-9), 141.9 (C-10), 132.8 (C-1'), 129.2 (C-2', 6'), 113.8 (C-3', 5'), 157.5 (C-4'), 54.9 (4'-OCH_3), 35.9 (C-1"), 29.5 (C-2"), 99.7 (Glc-C-1), 73.1 (Glc-C-2), 76.4 (Glc-C-3), 69.5 (Glc-C-4), 77.1 (Glc-C-5), 60.5 (Glc-C-6).

Compound **23**: White powder (MeOH-$CHCl_3$); mp:235~240℃; ESI-MS m/z:168.77 $[M-H]^-$; ^{1}H-NMR (500 MHz, DMSO-d_6) δ_H 12.11 (1H, s, -COOH), 9.14 (2H, s, -OH), 8.80 (1H, s, -OH), 6.90 (2H, s, 2, 6-H).

Compound **24**: Pale yellow feather crystal (MeOH-$CHCl_3$); mp:210~213℃; ESI-MS m/z:164.76 $[M+H]^+$; ^{1}H-NMR (300 MHz, DMSO-d_6) δ_H 12.09 (1H, s, -COOH), 9.93 (1H, s, 4-OH), 7.51 (2H, d, *J* = 8.4 Hz, 2, 6-H), 6.79 (2H, d, *J* = 8.4 Hz, 3, 5-H), 7.50 (1H, d, *J* = 15.9 Hz), 6.28 (1H, d, *J* = 15.9 Hz).

Compound **25**: White powder (MeOH-$CHCl_3$); mp:255~257℃; ESI-MS m/z:166.79 $[M-H]^-$; ^{1}H-NMR (300 MHz, DMSO-d_6) δ_H 12.47 (1H, s, -COOH), 9.82 (1H, s, 3-OH), 3.83 (3H, s, 4-OCH_3), 7.46 (2H, brs), 6.87 (1H, d, *J* = 8.7 Hz).

Compound **26**: White powder (MeOH-$CHCl_3$); mp:214~216℃。ESI-MS m/z:136.73$[M-H]^-$, ^{1}H-NMR (300 MHz, DMSO-d_6) δ_H 12.39 (1H, s, -COOH), 10.20 (1H, s, 4-OH), 7.80 (2H, d, *J* = 8.6 Hz, 2, 6-H), 6.84 (2H, d, *J* = 8.6 Hz, 3, 5-H).

Compound **27**: Light yellow needle crystal (MeOH-$CHCl_3$); mp:197~200℃; ESI-MS m/z:152.68 $[M-H]^-$; ^{1}H-NMR (300 MHz, DMSO-d_6) δ_H 12.29 (1H, s, 1-COOH), 9.60 (1H, s, 3-OH), 9.31 (1H, s, 4-OH), 7.33 (1H, d, *J* = 1.9 Hz, 2-H), 7.28 (1H, dd, *J* = 8.2, 1.9 Hz, 6-H), 6.77 (1H, d, *J* = 8.2 Hz, 5-H).

Compound **28**: White powder (MeOH-$CHCl_3$); mp:180~182℃; ESI-MS m/z:878.80$[M+Cl]^-$, 844.58 $[M+H]^+$; ^{1}H-NMR (300 MHz, C_5D_5N) δ_H 0.89 (6H, t, *J* = 6.7 Hz, -CH_3×2), 4.96 (1H, d, *J* = 7.6 Hz, H-1"), 4.36 (1H, m, Ha-6"), 4.48 (1H, brs, Hb-6"), 4.55 (1H, m, 1-Ha), 4.71 (1H, dd, *J* = 10.5, 6.7 Hz, 1-Hb), 5.29 (1H, m, 2-H), 4.31 (1H, m, 3-H), 4.21 (1H, m, 4-H), 4.56 (1H, m, 2'-H), 8.55 (1H, d, *J* = 9.0 Hz, N-H), 5.46 (1H, m, 9-H), 5.56 (1H, m, 8-H); ^{13}C-NMR (75 MHz, C_5D_5N) δ_C 70.8 (C-1), 52.1 (C-2), 76.3 (C-3), 72.8 (C-4), 28.0 (C-7), 130.8 (C-8Z), 130.6 (C-9Z), 28.3 (C-10), 105.9 (C-1"), 75.5 (C-2"), 78.8 (C-3"), 71.9 (C-4"), 78.9 (C-5"), 63.0 (C-6"), 176.0 (C-1'), 72.9 (C-2'), 35.9 (C-3'). δ_C 34.4, 32.5, 30.5, 30.4, 30.3, 30.2, 30.0, 27.2, 26.2, 23.3 (CH_2), 14.6 (CH_3).

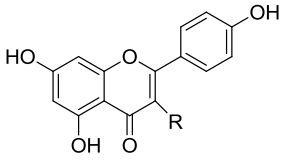
Compound **29**: Light yellow needle crystal (Petroleum ether-Ethyl acetate); mp:173~175℃; ESI-MS m/z:683.20 $[M+H]^+$; ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H 16.16 (1H, s, -OH), 15.97 (1H, s, -OH), 15.62 (1H, s, -OH), 10.72 (1H, s, -OH), 10.69 (1H, s, -OH), 9.69 (1H, s, -OH), 9.26 (1H, s, -OH), 3.82 (4H, s, Ar-CH_2-Ar×2), 3.86(1H, m), 3.72 (6H, s, Ar-OCH_3×2), 2.11 (6H, s, Ar-CH_3×2). δ_H 0.99 (6H, t, *J* = 7.3 Hz), 1.75 (4H, m), 3.09 (4H, m) 2×-$COCH_2CH_2CH_3$, δ_H 0.91 (3H, t, *J* = 7.4Hz), 1.16 (3H, d, *J* = 6.4 Hz), 1.84 (1H, m), 1.14 (1H, m), 3.86 (1H, m) -$COCH(CH_3)CH_2CH_3$.

Compound **30**: Light yellow needle crystal (Petroleum ether-Ethyl acetate); mp 147~149 ℃;

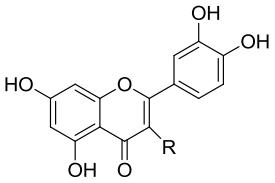
ESI-MS m/z:655.10 $[M+H]^+$; ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H 16.16 (1H, s, -OH), 15.95 (1H, s, -OH), 15.61 (1H, s, -OH), 10.69 (1H, s, -OH), 9.64 (2H, s, -OH), 9.27 (1H, s, -OH), 3.83 (4H, s, Ar-CH_2-Ar×2), 3.73 (6H, s, Ar-OCH_3×2), 2.12 (6H, s, Ar-CH_3×2). δ_H 3.10 (1H, m), 1.26 (3H, brs), 1.00 (3H, d, *J* = 7.3 Hz) -COCH(CH_3)-CH_3, δ_H 3.10 (1H, m), 1.75 (2H, m), 0.92 (3H, t, *J* = 7.4Hz), 1.17 (3H, d, *J* = 7.2 Hz) -COCH(CH_3)CH_2-CH_3, δ_H 2.73 (3H, s) -$COCH_3$。

Compound **31**: White powder (Acetone); mp:102~103℃; ESI-MS m/z:348.29 $[M+NH_4]^+$, 329.25$[M-H]^-$; ^{1}H-NMR (500 MHz, C_5D_5N) δ_H 6.38 (1H,dd, *J* = 5.7, 15.9 Hz, 10-H), 6.33 (1H, dd, *J* = 5.4, 15.3 Hz, 9-H), 4.50 (2H, m, 8, 11-H), 3.94 (1H, m, 12-H), 2.50 (2H, m, 2-H), 0.85 (3H, m, 18-H); ^{13}C-NMR (125 MHz, C_5D_5N) δ_C 177.4 (C-1), 137.0 (C-10), 131.3 (C-9), 76.6 (C-11), 75.6 (C-8), 72.3 (C-12), 14.6(C-18), 23.4~38.9 (-CH_2-).

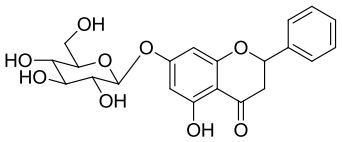
2. Structures of the isolated compounds



1 R=*O*-(6-p-coumaroyl)-*β*-D-Glc
4 R=H
7 R=*O*-*α*-L-Ara
8 R=OH
10 R=*O*-(6-*O*-acetyl)-*β*-D-Glc



2 R=OH
3 R=H
12 R=*O*-*α*-L-Rha
14 R=*O*-*β*-D-Glc



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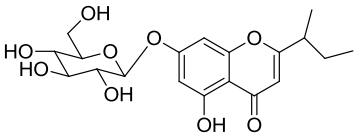

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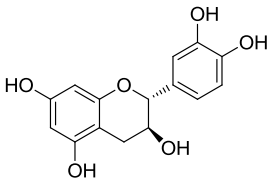

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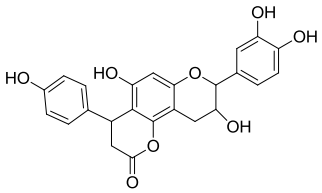

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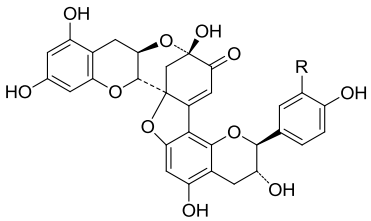

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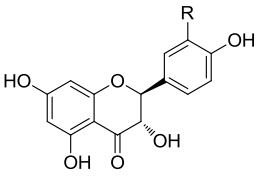
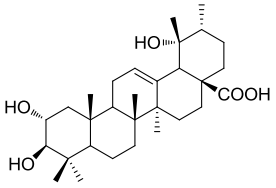


15 R=-H
16 R=-OH



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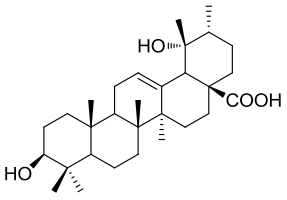

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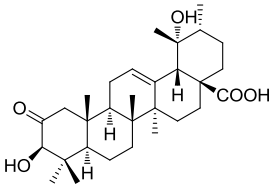

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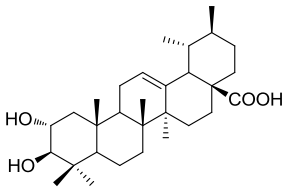

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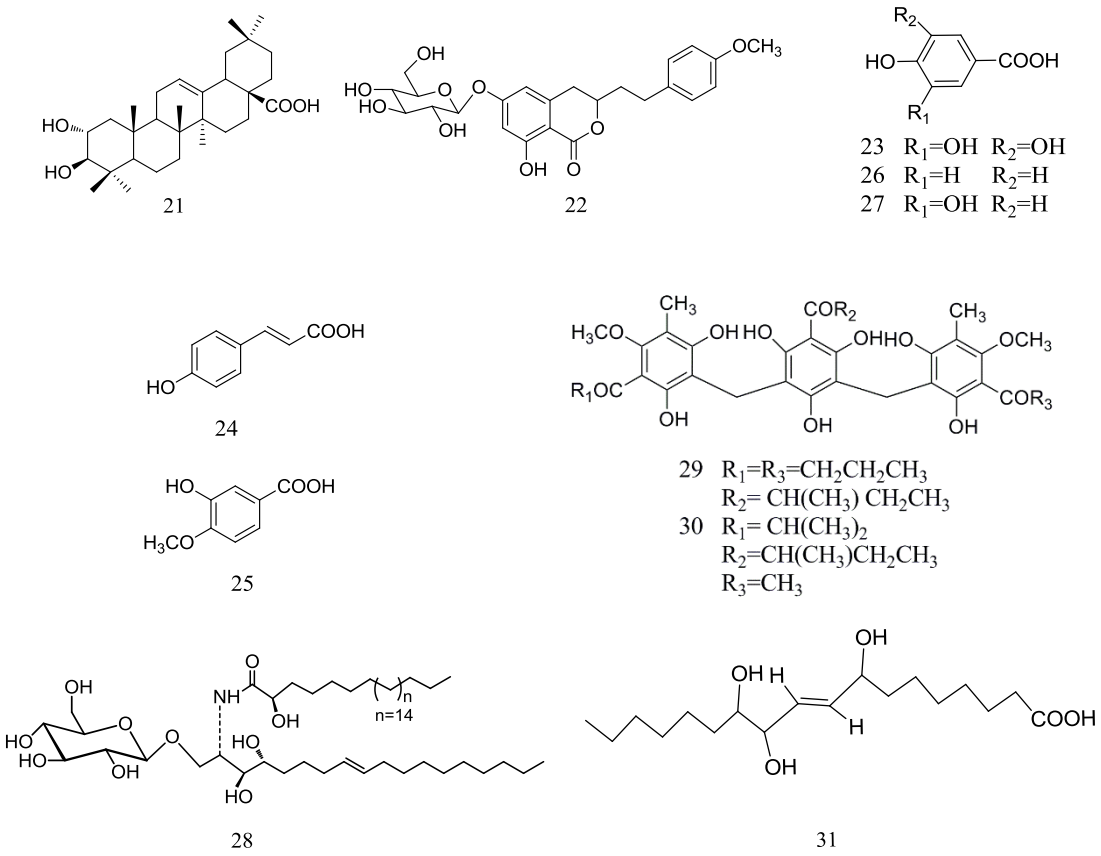

Fig. S1. Structures of compounds **1-31**