TRITERPENE SAPONINS AND OTHER CONSTITUENTS FROM *Fatsia japonica*

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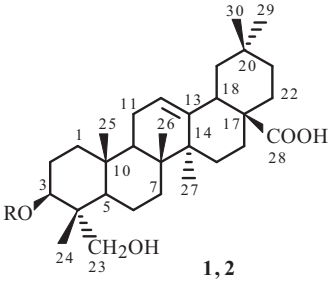
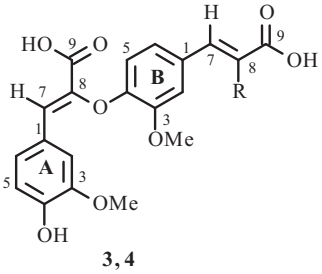
Fatsia japonica Decne. (Araliaceae) is used in eastern folk medicine [1]. Various class of compounds such as triterpene saponins [2–5], squalene, fatty acids and their methyl esters [6], anthocynanins [7], and sterols [6] and their glycosides [8] have been isolated from this plant.

Shade air-dried and powdered roots (16.3 kg) and mature fruits (425.0 g) of *F. japonica* were extracted with 95% ethanol. Dried EtOH extracts of roots (752.2 g) and fruits (58.9 g) were dissolved in water and fractionated with *n*-hexane, dichloromethane, and ethyl acetate. The dichloromethane- soluble fraction (139.0 g) of *F. japonica* root produced some precipitate, which was filtered to give two fractions, FRD-1 (precipitate) and FRD-2 (filtrate). FRD-1 on a silica gel column ($CHCl_3$–MeOH 7:1) gave compound **1** (415 mg). On the other hand, fraction FRD-2 on a Sephadex LH-20 column (MeOH) gave four fractions, FRD-2-1 to FRD-2-4. Fraction FRD-2-2 (20 g) on a silica gel column ($CHCl_3$–MeOH 20:1) gave 15 fractions, FRD-2-2-1 to FRD-2-2-15. Separate column chromatography of FRD-2-2-6, FRD-2-2-9, and FRD-2-2-10 on Sephadex LH-20 columns using acetone as an eluent yielded compounds **4** (90 mg), **3** (350 mg), and **7** (50 mg), respectively. The EtOAc-soluble fraction of *F. japonica* fruit (6 g) was chromatographed on a Sephadex LH-20 column using MeOH as eluent to give five fractions, FFE-I to FFE-V. Fraction FFE-I was further chromatographed on a silica gel column using $CHCl_3$–MeOH (7:1, v/v) as eluent to yield nine fractions, FFE-I to FFE-IX. Separate preparative TLC of fractions FFE-I-II and FFE-I-VIII in $CHCl_3$–MeOH (5:1, v/v) and fractions FFE-I-IV in a solvent system of $CHCl_3$–MeOH–H_2O (15:6:0.6, v/v/v) gave compounds **1** (40 mg), **5** (20 mg), and **2** (190 mg), respectively. The shade air-dried and powdered wood (4.7 kg) of *F. japonica* was extracted with acetone. The dried acetone extract of wood was dissolved in water and fractionated with *n*-hexane, dichloromethane, and ethyl acetate. The EtOAc-soluble fraction of *F. japonica* wood (2.12 g) on a Sephadex column (MeOH–EtOH, 1:1, v/v) gave four fractions. Fraction 3 (114.5 mg) was further purified on a silica column using benzene–MeOH (5:1, v/v) as eluent to give compound **6** (64.2 mg).

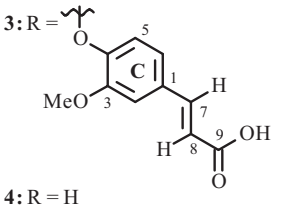


1, 2

1: R = α-L-Ara*p*
2: R = β-D-Glc*p*

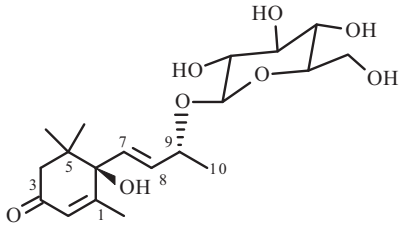


3, 4



3: R =

4: R = H



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The structures of isolated compounds (**1–7**) were determined by their detailed spectral analysis, mainly EI-MS, FAB-MS, 1D NMR (^{1}H, ^{13}C and DEPT), and 2D NMR (COSY, NOESY, TOCSY, HMQC and HMBC), as well as by comparison of their spectral data with those of related compounds.

3-*O*-α-L-Arabinopyranosyl-hederagenin (1). White powder, mp 238–240°C. $C_{35}H_{56}O_8$, FAB-MS: *m/z* 603 $[M - H]^-$ [1].

3-*O*-β-D-Glucopyranosyl-hederagenin (2). White powder,mp 246–247°C. $C_{36}H_{58}O_9$, EI-MS: *m/z* 633 $[M - H]^-$ [9].

8-*O*-4/8-*O*-4-Dehydrotriferulic Acid (3). Brown solid, mp 170–172°C. $C_{30}H_{26}O_{12}$, EI-MS: *m/z* 578 $[M]^+$, PMR spectrum (500 MHz, MeOD, δ, ppm, J/Hz): 3.58 (3H, s, A3-OMe), 3.77 (3H, s, B3-OMe), 3.96 (3H, s, C3-OMe), 6.35(1H, d, J = 16.0, C8-H), 6.72 (1H, d, J = 8.5, B5-H), 6.73 (1H, d, J = 8.5, A5-H), 6.78 (1H, d, J = 8.5 Hz, C5-H), 7.05 (1H, dd, J = 8.5, 2.5, C6-H), 7.06 (1H, dd, J = 8.5, 2.5, A6-H), 7.10 (1H, dd, J = 8.5, 2.5, B6-H), 7.31 (1H, d, J = 2.0, C2-H), 7.35 (1H, d, J = 2.0, A2-H), 7.37 (1H, s, A7-H), 7.39 (1H, s, B7-H), 7.59 (1H, d, J = 2.0, B2-H), 7.60 (1H, d, J = 16.0, C7-H). ^{13}C NMR spectrum (125 MHz, MeOD, δ, ppm): 55.91 (A3-OMe), 56.28 (B3-OMe), 56.73 (C3-OMe), 112.74 (C-2), 113.73 (A-2), 114.36 (C-5), 114.64 (B-5), 114.82 (B-2), 116.20 (A-5), 117.81 (C-8), 123.19 (C-6), 125.56 (B-6), 125.71 (A-1), 126.52 (A-6), 128.11 (B-7), 128.45 (B-1), 129.13 (A-7), 130.66 (C-1), 138.65 (A-8), 140.18 (B-8), 146.01 (C-7), 148.58 (A-3), 148.85 (B-4), 149.14 (C-4), 149.81 (A-4), 150.04 (B-3), 150.49 (C-3), 166.55 (B-9), 166.78 (A-9), 170.59 (C-9) [10].

8-*O*-4-Dehydrodiferulic Acid (4). Brown crystalline powder, mp 208–210°C. $C_{20}H_{18}O_8$, EI-MS: *m/z* 386 $[M]^+$, PMR spectrum (500 MHz, MeOD, δ, ppm, J/Hz): 3.71 (3H, s, A3-OMe), 3.98 (3H, s, B3-OMe), 6.39 (1H, d, J = 16.0, B8-H), 6.76 (1H, d, J = 8.5, A5-H), 6.81 (1H, d, J = 8.5, B5-H), 7.07 (1H, dd, J = 8.0, 2.0, B-6H), 7.11 (1H, dd, J = 8.0, 2.0, A-6H), 7.33 (1H, d, J = 2.0, A7-H), 7.39 (1H, s, B-2H), 7.44 (1H, d, J = 2.0, A2-H), 7.61 (1H, d, J = 16.0, B7-H). ^{13}C NMR spectrum (125 MHz, MeOD, δ, ppm): 56.04 (A3-OMe), 56.74 (B3-OMe), 112.71 (B-2), 113.84 (A-2), 114.74 (B-5), 116.22 (A-5), 117.80 (B-8), 123.22 (B-6), 125.74 (A-1), 126.40 (A-6), 128.82 (A-7), 130.53 (B-1), 139.20 (A-8), 146.10 (B-7), 148.92 (A-3), 149.40 (B-4), 149.80 (A-4), 150.53 (B-3), 167.03 (A-9), 170.67 (B-9) [11].

(6*R*,9*R*)-Roseoside (5). White powder, $C_{19}H_{30}O_8$, FAB-MS: *m/z* 385 $[M - H]^-$, PMR spectrum (500 MHz, C_5D_5N, δ, ppm, J/Hz): 1.14 (3H, s, H-11), 1.21 (3H, s, H-12), 1.37 (3H, d, J = 6.0, H-10), 2.00 (3H, d, J = 1.0, H-13), 2.35 (1H, d, J = 16.5, H-4a), 2.65 (1H, d, J = 16.5, H-4b), 3.80 (1H, m, H-5′), 3.89 (1H, m, H-2′), 3.99 (1H, t, J = 9.0, H-4′), 4.10 (1H, t, J = 9.0, H-3′), 4.16 (1H, dd, J = 11.5, 6.5, H-6b), 4.43 (1H, dd, J = 11.5, 2.0, H-6a), 4.69 (1H, m, H-9), 4.84 (1H, d, J = 8.0, H-1′), 6.04 (1H, s, H-2), 6.10 (1H, d, J = 15.5, H-7), 6.24 (1H, dd, J = 15.5, 6.5, H-8). ^{13}C NMR spectrum (125 MHz, C_5D_5N, δ, ppm): 18.84 (C-13), 20.70 (C-10), 22.90 (C-11), 24.10 (C-12), 41.17 (C-5), 49.77 (C-4), 62.23 (C-6′), 71.14 (C-4′), 74.61 (C-2′), 75.78 (C-9), 77.79 (C-3′, C-5′), 78.42 (C-6), 102.21 (C-1′), 126.36 (C-2), 130.79 (C-7), 134.24 (C-8), 164.10 (C-1), 197.80 (C-3) [12].

Oxyresveratrol (6). Yellowish crystal, mp 200–201°C. $C_{14}H_{12}O_4$, EI-MS: *m/z* 244 $[M]^+$, PMR spectrum (500 MHz, MeOD, δ, ppm, J/Hz): 6.15 (1H, t, J = 2.0, H-4), 6.35 (2H, m, H-3′, H-5′), 6.44 (2H, m, H-2, H-6), 6.81 (1H, d, J = 16.5, H-8), 7.26 (1H, d, J = 16.5, H-7), 7.32 (1H, d, J = 6.0, H-6′). ^{13}C NMR spectrum (125 MHz, MeOD, δ, ppm): 102.3 (C-4), 102.29 (C-3′) 105.66 (C-2, C-6), 108.39 (C-5′), 117.87 (C-1′), 124.83 (C-7), 126.53 (C-8), 128.39 (C-6′), 142.18 (C-1), 157.32 (C-2′), 159.22 (C-4′), 159.56 (C-3, C-5) [13].

Protocatechuic Acid (7). Brown crystal, mp 198–200°C. $C_7H_6O_4$, EI-MS: *m/z* 154 $[M]^+$, PMR spectrum (500 MHz, Me_2CO, δ, ppm, J/Hz): 6.92 (1H, d, J = 8.5, H-5), 7.50 (1H, dd, J = 8.5, 2.0, H-6), 7.55 (1H, d, J = 2.0, H-2). ^{13}C NMR spectrum (125 MHz, Me_2CO, δ, ppm): 115.63 (C-5), 117.40 (C-2), 123.04 (C-6), 123.57 (C-1), 145.41 (C-3), 150.59 (C-4), 167.77 (C-7) [14].

Compounds **3–6** were obtained for the first time in the family Araliaecae, while compound **7** was reported for the first time from the genus *Fatsia*. Compounds **1** and **2** are very common in *F. japonica*. The presence of compounds **3–6** in the family Araliaceae is very unusual and may constitute an index for chemotaxonomic characterization of the genus.

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